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**VERIFICATION OF THE
PROPERTIES OF NEW NON-AZEOTROPIC
FLUID MIXTURES**

(Part of the program of the
Federal Panel on Energy R&D [PERD])

**FINAL REPORT
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SUMMARY

New refrigerants and refrigerant mixtures are becoming increasingly important in the HVAC & R industry due to the ozone depletion problem and the banning of ozone depleting CFCs. These new refrigerants, especially the refrigerant mixtures, can also provide an increase in system COPs and/or capacities. The lack of knowledge of the thermodynamic properties of these substances prompted CRIQ to assemble a vapour-liquid equilibrium apparatus. This apparatus can supply the necessary experimental data required by the Carnahan-Sterling-DeSantis equation of state to model a substance. A series of tests were performed on the CRIQ apparatus for 4 pure substances (R-22, R-114, R-142b, R-152a) and three mixtures (R-22/R-114, R-22/R-142b, R-22/R-152a). The results of these tests showed some deviation from results reported elsewhere but given the uncertainty of the experimental results these differences are not significant. A sensitivity analysis was performed and demonstrated that the CSD parameters are very sensitive to the pressure measurement accuracy.

RÉSUMÉ

Les nouveaux réfrigérants ainsi que les mélanges de réfrigérants deviennent de plus en plus important dans l'industrie du CVAC & R. Ce phénomène est attribuable au problème de la déplétion de l'ozone et de la réglementation subséquente des CFC dommageables. Ces nouveaux réfrigérants, plus particulièrement les mélanges, peuvent aussi amener une augmentation des COP et de la capacité des systèmes. Cependant, le manque de connaissance des propriétés thermodynamiques de ces fluides pose un problème important. Afin de répondre à ce problème, le CRIQ a conçu et assemblé un appareil d'équilibre vapeur-liquide. Cet appareil permet de recueillir les informations expérimentales pour simuler ces nouveaux fluides à l'aide de l'équation d'état de Carnahan-Starling-DeSantis. Une série de tests ont été effectués sur cet appareil pour 4 réfrigérants purs (R-22/R-114, R-22/R-142b, R-22/R-152a) et 3 mélanges (R-22/R-114, R-22/R-142b, R-22/R-152a). Les résultats de ces tests montrent certaines différences comparées à ceux mesurés par d'autres groupes mais étant donné l'incertitude associée à ces résultats, on peut conclure que ces différences ne sont pas significatives. Une analyse de sensibilité a été effectuée et les résultats démontrent que l'équation d'état CSD est très sensible à la précision de la mesure de pression.

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NOMENCLATURE

- a: Parameter used in Equ. (1), a measure of molecular interactions.
- A_0, A_1, A_2 : Coefficients of Equ. (2) used to model the temperature dependency of "a".
- a_1 : "a" parameter for pure substance 1. Equ. (5).
 a_2 : "a" parameter for pure substance 2. Equ. (5).
 a_{12} : Combination of parameter a_1 and a_2 as defined in Equ. (7).
- b: Parameter used in Qua. (1), a measure of the average closest distance of approach of molecules.
- B_0, B_1, B_2 : Polynomial coefficients of Equ. (3) used to model the temperature dependency of "b".
- b_1 : "b" parameter for pure substance 1. Equ. (6).
 b_2 : "b" parameter for pure substance 2. Equ. (7).
 b_{12} : combination of parameter b_1 and b_2 as defined in Equ. (8).
 f_{12} : Empirical factor, determined from VLE experimental data, used in computing a_{12} , Equ. (7).
- P: Refrigerant pressure.
R: Ideal gas constant.
T: Refrigerant temperature.
 T_c : Critical temperature.
V: Refrigerant specific volume.
 w_1, w_2 : Molar fractions of substance 1 and 2.
 w_e, w_p : Weighting factor for minimization equations. Equ. (4) & (9).
X: Molar composition of the more volatile compound in a mixture.
 σ : Standard deviation.
 r : Minimization functions defined by Equ. (4) & (9).

SUBSCRIPTS :

- c: Variables computed using the equation of state.
e: Experimental values.
L: Saturated liquid values.
Sat: Variables evaluated at saturation point.

1.0 INTRODUCTION

The advent of the Montreal Protocol limiting, and eventually eliminating, the production of ozone depleting chlorofluorocarbons (CFCs) has triggered an urgent need in the refrigeration and air conditioning industry for replacement alternatives.

There is no doubt in the scientific community and in the industry that substitutes for the banned CFCs will be found but there is also a strong consensus that those replacements will compromise some of the qualities and properties possessed by the current refrigerants. In some instances, the use of substitutes, such as non-azeotropic mixtures for example, can enhance the performances of an installation but in other cases the use of a substitute might require hardware changes that could have important consequences for the industry. Therefore, it becomes essential to acquire full knowledge of the properties of these new refrigerants so that their impact on system performances and on hardware can be estimated.

To fulfill that need and expand its expertise in fluid and system modeling, CRIQ has undertaken work in order to determine the properties of alternative refrigerants.

Accordingly, CRIQ has assembled an apparatus for the observation of phase equilibria in pressurized fluids. This commitment has resulted in a 30 000,\$ investment by CRIQ to design and construct this unique apparatus, which is described in the following sections.

This report describes how the Vapour-Liquid Equilibrium (VLE) measurement apparatus is used to determine experimentally the interaction parameter, as defined in the Carnahan-Starling-Desantis (CSD) [1] equation of state, for the following mixtures :

R-22/R-152a ;
R-22/R-142b .

It is also shown that this apparatus can be used to determine experimentally the "a" and "b" coefficients, as defined in the CSD equation of state, for the following pure substances :

R-22 ;
R-142b ;
R-152a .

2.0 THEORY

2.1 EQUATION OF STATE

As described by Morrison and McLinden [1], the thermodynamic properties of a pure fluid or mixture can be determined by the use of an equation of state based on a realistic physical model which requires a minimum amount of experimental information.

The equation of state used in their report [1] for the calculation of state properties is the following :

$$\frac{PV}{RT} = \frac{1 + Y + \frac{Y^2}{(1-Y)^3} - Y^3}{1} - \frac{a}{RT(V+b)} \quad (1)$$

$$\text{where } Y = b/4V$$

This equation was first suggested by Carnahan-Starling [2], and modified by DeSantis [3], and exhibited good agreement for simple inorganic molecules, hydrocarbons and their mixtures. Morrison [4] later used this equation to determine refrigerant mixtures properties. The advantages of this equation of state are: its ability to model high density fluids (liquids) compared to other equations of state, its simplicity, the fact that it is based on a good physical model, and its capabilities in modelling refrigerants, which are mostly small, nearly spherical molecules.

On a molecular basis, an equation of state has to be able to model high density fluid and to take into consideration the attraction forces between molecules at moderate and large distances as well as their repulsion forces at short distances. Hence, in equation (1), the first term represents the hard-sphere fluid model where the "b" parameter is defined as an effective core that is a measure of the average closest distance of approach of molecules. The second term of this equation represents the attraction phenomena between molecules and the "a" parameter is a measure of these molecular interactions. Both parameters are temperature dependant and in this work are represented, for pure substances, by the following forms :

$$a = A_0 \exp (A_1 T + A_2 T^2) \quad (2)$$

$$b = B_0 + B_1 T + B_2 T^2 \quad (3)$$

The "a" and "b" parameters have to be determined experimentally. Their values are obtained through the minimization of the differences between measured state properties and those calculated using the equation of state (1). The following properties are used in the minimization process: - liquid volume,
- saturation pressure.

The minimization function is defined as follow :

$$\left[(a,b,T) = \frac{W_e (V_{1,e} - V_{1,c})^2}{(V_{1,e})^2} + \frac{W_p (P_{sat,e} - P_{sat,c})^2}{(P_{sat,e})^2} \right] \quad (4)$$

where e = experimental values;

c = calculated values (by equation 1);

W_e, W_p = weighting factors (adjusted to match reliability).

In this work, the weighting factors W_p and W_e are both set to 1. Therefore, this process is iterative since we need values for "a" and "b" in equation (1).

This equation of state can also be applied to refrigerant mixtures by the use of a proper mixing rule to determine the "a" and "b" parameters. That is to say that there exists an effective "a" and "b" such that equation (1) used for pure materials can also be used for mixtures. In this work, the mixing models for "a" and "b" are as follows:

$$a = W_1^2 a_1 + 2 W_1 W_2 a_{12} + W_2^2 a_2 \quad (5)$$

$$b = W_1^2 b_1 + 2 W_1 W_2 b_{12} + W_2^2 b_2 \quad (6)$$

where :

a_1, a_2 : "a" parameters for the pure materials 1 and 2;

b_1, b_2 : "b" parameters for the pure materials 1 and 2;

W_1, W_2 : molar fraction of material 1 and 2;

The a_{12}, b_{12} parameters are defined as :

$$a_{12} = (1-f_{12}) (a_1 a_2)^{1/2} \quad (7)$$

$$b_{12} = [(b_1^{1/3} + b_2^{1/3})/2]^3 \quad (8)$$

where f_{12} is defined as the interaction parameter and has to be computed from experimental data. The approach is again to find the value of f_{12} which minimizes the sum of squares of relative deviations between measured and calculated quantities :

$$\left[(T, x_e, f_{i,ii}) = \frac{W_p (P_{sat,e} - P_{sat,c})^2}{(P_{sat,e})^2} + \frac{W_e (V_{l,e} - V_{l,c})^2}{(V_{l,e})^2} \right] \quad (9)$$

where,

x_e = liquid molar composition (more volatile compound).

As in the case of equation (4), the solution procedure is iterative.

Equations (4) and (9) presented here include 2 experimental parameters, which have to be determined experimentally.

2.2 EXPERIMENTAL METHOD

In the previous section, it was demonstrated that experimental data were required to determine the state properties of pure fluid or mixture when using the CSD equation of state. The methods for the direct determination of equilibrium data can be classified for the most part into the following groups [5] :

- 1- distillation method;
- 2- circulation method;
- 3- static method;
- 4- dew and bubble point method;
- 5- flow method.

Further to discussion with scientists at the National Institute of Standards and Technology [6] the dew and bubble point method was selected as the more appropriate one to work with refrigerants. This method will now be described in detail along with a brief description of the four other techniques.

2.2.1 Distillation method

This is the oldest method presented here. It is used for the determination of the vapor-liquid equilibrium by determining the concentration of both phases analytically.

In this method, we distill off a small amount of liquid from a boiling flask which contains a large charge. Therefore, the liquid composition stays constant and the vapor composition can be found analytically. Large errors can be caused by condensation of vapour on the cold walls of the distillation flask. This method is very seldom used today.

2.2.2 Circulation method

This method is widely used for the determination of equilibrium data and even though there is a wide variety of stills using this technique, they are all based on a common principle, as shown in fig. 1.

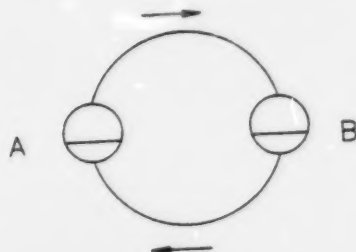


Fig. 1 Circulating stills

The vapors evolve from the boiling mixture in the distilling flask A, pass through the vapour conduit and after complete condensation collect in the receiver B. After filling the receiver, the condensate returns to the distilling flask. It can be shown that the liquid in flask B will be of the same composition as the vapor in flask A, therefore allowing the determination of the vapor-liquid equilibrium. This demonstration, however, is beyond the scope of this study.

2.2.3 Static method

In this method, the solution is charged into a closed and evacuated cylinder which is placed in a thermostat. The cylinder is then agitated until equilibrium is established. Samples of the vapor and liquid phases are then removed for analytical analysis. This method is not as simple as it appears, since removing the gas sample causes great difficulties. At low and moderate pressure a large portion of the gas has to be removed for analysis, thus causing a disturbance in the equilibrium. For this reason the static method is not often used at these pressures.

2.2.4 Flow method

In the flow method, an equilibrium chamber filled with a liquid of known composition is fed a constant stream of vapor of fixed composition. The vapor passes through the liquid and portion of it condensates, the rest being evacuated outside the chamber. When steady state is achieved the liquid level in the chamber stabilizes, thus no more vapor condensates in the liquid. The vapor coming out of the chamber is therefore in equilibrium with the liquid and analytical determination of both phases can be performed.

2.2.5 Dew and bubble point method

This method was selected for the experimental measurements required in this work. An apparatus utilizing this technique has been built at CRIQ.

The principle of this method is different than that of the four previous ones as can be seen in Figure 2, which shows a Pressure-composition equilibrium diagram.

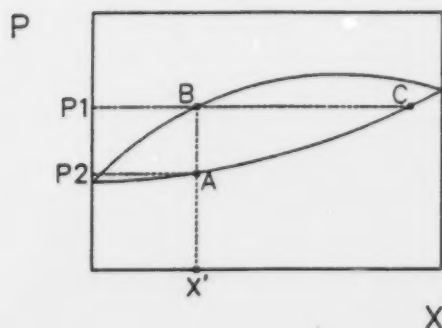


Fig. 2 Equilibrium diagram

All the previous methods used pairs of points on horizontal segments (BC) to determine the equilibrium curves. It is also possible to obtain these curves by determining points on vertical segments (AB). These segments describe the behaviour of mixtures of constant composition at variable pressure and constant temperature. Based on this principle, it is possible to develop a methodology to determine the A and B points.

For a sample of composition X' at some pressure higher than P_1 , the whole sample is then in a liquid phase. When the pressure is lowered to P_1 , an infinitesimal amount of vapor is formed which is in equilibrium with the liquid. This point (B) is called the "bubble point" of the mixture. If the pressure is then lowered to P_2 , all the liquid is vaporized except for an infinitesimal amount which is in equilibrium with the vapor. This point (A) is called the "dew point" of the mixture. In practice, we do not find directly the dew or bubble point, given the difficulty in judging when a sample is either all saturated vapor or liquid.

For example, in the case of the bubble point, the sample is gradually pressurized from a pressure below P_1 , where a visible portion of the mixture is in the vapor phase, to a pressure very close to P_1 , but where it is still possible to measure the amount of vapor left in the sample. From these measurements, it is possible to extrapolate the location of the bubble point. A similar approach is adopted for the dew point.

This process will yield the saturation pressure and liquid and/or vapor molar volume for the given temperature and composition. These are the only experimental data required by the CSD equation of state.

3.0 DESCRIPTION OF THE APPARATUS

The VLE apparatus developed at CRIQ will serve to determine the bubble point of the mixture. This information is sufficient to obtain the parameters required by the CSD equation of state.

As shown in Figure 3, the apparatus consists of a tubular sapphire optical cell immersed in a constant temperature bath. This cell contains the sample to be tested. The bath temperature is accurately determined with a platinum resistance thermometer. The temperature level is maintained constant using a $\pm 0.01^\circ\text{C}$ temperature controller linked to a cooling and a heating unit. The pressure in the sapphire tube is measured with a "Bailey" pressure transducer which has its outlet located at the bottom of the tube. The volume in the sapphire cell is varied using a mercury pump.

Liquid and vapor volumes are obtained by measuring the liquid and mercury meniscus positions with a digital micrometer.

The refrigerant sample is initially inserted in a stainless steel tube, located between valves 2 and 3 on Figure 3. The mass of refrigerant inserted in the system is obtained through measurements of the empty and filled stainless steel tube on a precision scale.

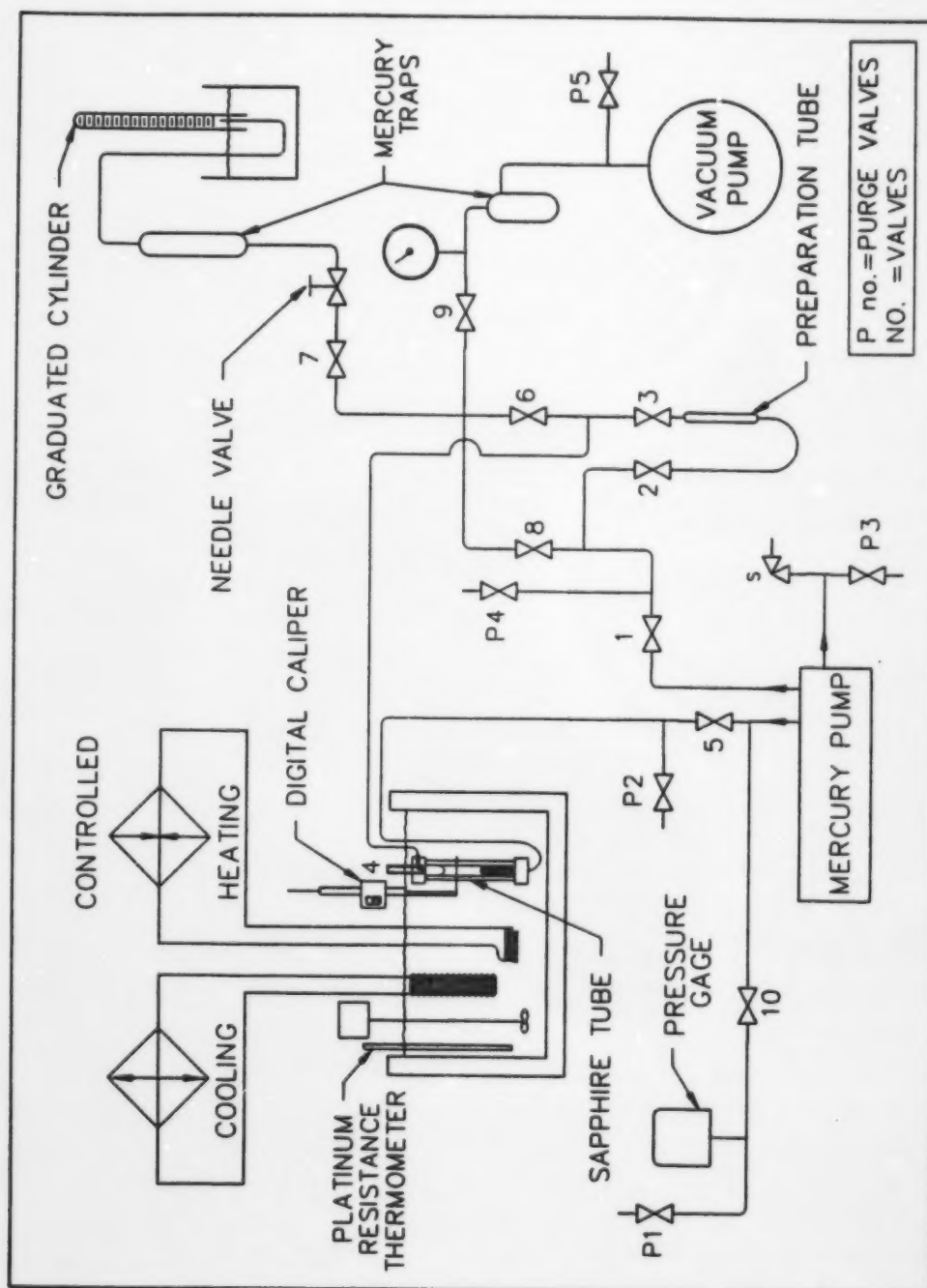


Figure 3 : Vapor-Liquid Equilibrium apparatus

The apparatus is evacuated before any experiment with a 3/4 hp vacuum pump. All the connections are made out of 1/16 in. stainless steel tubing and compression fittings.

A graduated cylinder is used to recover any refrigerant vapour that did not transfer from the preparation cell to the sapphire tube at the start of the experiment.

A data acquisition system is used to monitor the apparatus and take the pressure readings. A list of the various components of the apparatus is given in Table 1.

The photographs in Appendix A show the principal components of the apparatus.

- Nestlab Isothermal bath	: Temperature range : -25 to 80° C
- Guildline digital thermometer	: Model 9540 : $\pm 0,001^{\circ}$ C
- Bailley pressure transducer	: KA12111, $\pm 0,5\%$ of full scale Range 0 to 300 psig
- Digital micrometer	: Mitutoyo digimatic $\pm 0,0005$ in.
- Data logger	: HP 3497 A
- Computer	: HP 85
- Sapphire tube	: 1 cm ID, Saphikon Inc.
- Mercury pump	: Ruska manual pump
- Electronic weigh scale	: METTLER AE200, $\pm 0,0001$ g

Table 1 : Components of the VLE apparatus

4.0 EXPERIMENTAL PROCEDURE

With the apparatus described in Section 3.0, it is now possible to measure the bubble point properties of a pure substance or mixture by following a proper experimental procedure. Such a procedure was developed at CRIQ and will now be described.

The first step is to prepare the substance to be tested. In our work, two types of substance were considered: pure refrigerants and refrigerant mixtures. In the case of a pure substance, it is first required to clean the stainless steel preparation tube of any alien materials, such as mercury, that could have been left over from previous experiments. The tube is then evacuated and filled with a small amount of the substance to be tested, and once again the tube is evacuated. This procedure ensures that any gas left in the tube will consist entirely of the test substance. Following this, the tube is weighed. The refrigerant is then charged in the tube which is weighed once more. The difference between the two weights gives us the total amount of refrigerant charged in the tube. In the case of a mixture, two tubes are prepared following the same procedure, their respective weights are chosen to match a given mixture composition. The actual composition X_L is obtained from these weight measurements. The tubes are joined together with valves keeping the refrigerants apart, and

then one tube is immersed in liquid nitrogen. The valves are opened and the substance in the warm tube is transferred to the cold one by cryogenic pumping. The tubes are weighed again and the total mass and composition of the mixture is determined.

The tube containing the pure refrigerant or mixture can now be inserted on the apparatus, between valves 2 and 3 on Figure 3. With valves 2 and 3 closed, the system is evacuated. A small amount of refrigerant is inserted in the system and it is evacuated again. This operation is repeated three times in order to ensure that any left over gas in the system will be of the same nature as the one in the preparation tube. With valves 1, 2, 3 and 4 (Figure 3) opened, mercury is pumped through the line, pushing the refrigerant sample in the sapphire tube. The operation is completed when mercury drops appear at the top of the sapphire cell. Valve 4 is then closed. Any leftover vapor is flushed out of the system into the graduated cylinder, thus allowing for the calculation of the total mass of refrigerant transferred to the sapphire tube.

At this point, the actual measurements begin. The bath temperature is adjusted to the desired level and when steady state is achieved (≈ 30 min.), the data can be recorded. The following measurements are taken :

- bath temperature;
- sapphire tube pressure;
- liquid meniscus position;
- mercury meniscus position;
- atmospheric pressure;
- room temperature.

The sample is then compressed by using the mercury pump and measurements are taken again. This process is repeated four times until there is only a small, but visible, amount of vapor in the sapphire tube. The temperature is then set to another value and the same measurements are repeated.

From the measured quantities, it is possible to obtain the saturated liquid specific volume for each temperature setting.

The other parameters required by the CSD equation of state, namely P_{sat} , T , X_L , are also known experimentally. Therefore, the apparatus provides us with all the necessary data to calculate the interaction or the "a", "b" parameters needed by the CSD equation.

5.0 EXPERIMENTAL RAW DATA

Following the procedure described in Section 4.0, a complete series of tests was performed on 4 pure refrigerants and 3 mixtures. The composition used for the various mixtures are presented in Table 2.

PURE REFRIGERANTS	R-22	R-114	R-142-b	R-152 a
REFRIGERANT MIXTURES	R-22/R-114	R-22/R-142b	R-22/R-152a	
COMPOSITION (Fraction of R-22)	0.35	0.30	0.30	
	0.50	0.40	0.40	
	0.65	0.50	0.50	
		0.60*	0.60	
		0.70	0.70*	

* These runs had to be eliminated due to experimental difficulties

TABLE 2 : SUBSTANCES INVESTINGATED WITH VLE TEST APPARATUS

5.1 PURE REFRIGERANTS

The raw experimental results for the pure refrigerants are the saturation pressure P_e , the saturation temperature T_e , and the saturated liquid specific volume V_e . These results are plotted in Figures 4 through 7 and also shown in Tables 4-7 at the end of Section 6.1. The reduced temperature given on the X-axis of the graphics is defined as :

$$T_r = T_e/T_c \quad (10)$$

where T_c is the refrigerant critical temperature (given at the top of the figures).

A typical experimental run consists of 7 points selected in the -20° C to 60° C temperature range. For each experimental point 4 measurements are needed to extrapolate the bubble point of the substance (ref. Section 4.0). In the case of R-22 and R-152a, 2 runs were performed and the results (Fig. 4 and 7) show good repeatability of the experimental

method. Three runs were performed on the R-142b sample, (Figure 6), and here again the results show good repeatability. The experimental runs on the R-114 sample (Figure 5), comprise only 5 points due to the low pressure limit (200 kPa) imposed by pressure gage accuracy limitations. Temperature levels above 60° C were not used in order to avoid having mercury gas affecting the pressure readings.

EXPERIMENTAL RESULTS
REFRIGERANT: R22
CRITICAL TEMPERATURE (deg. C): 96.0

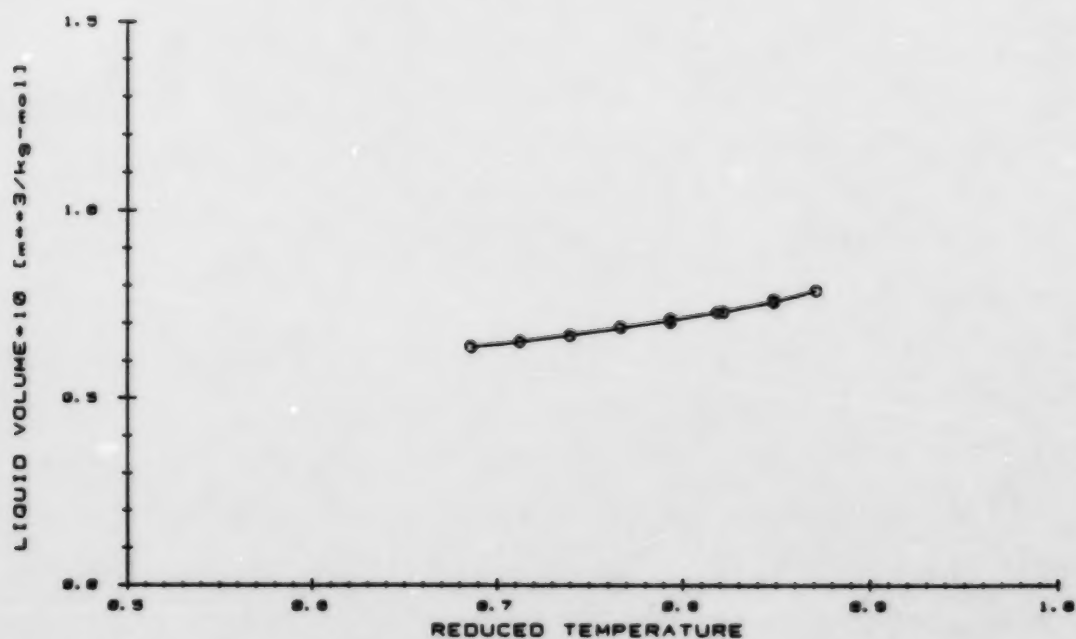
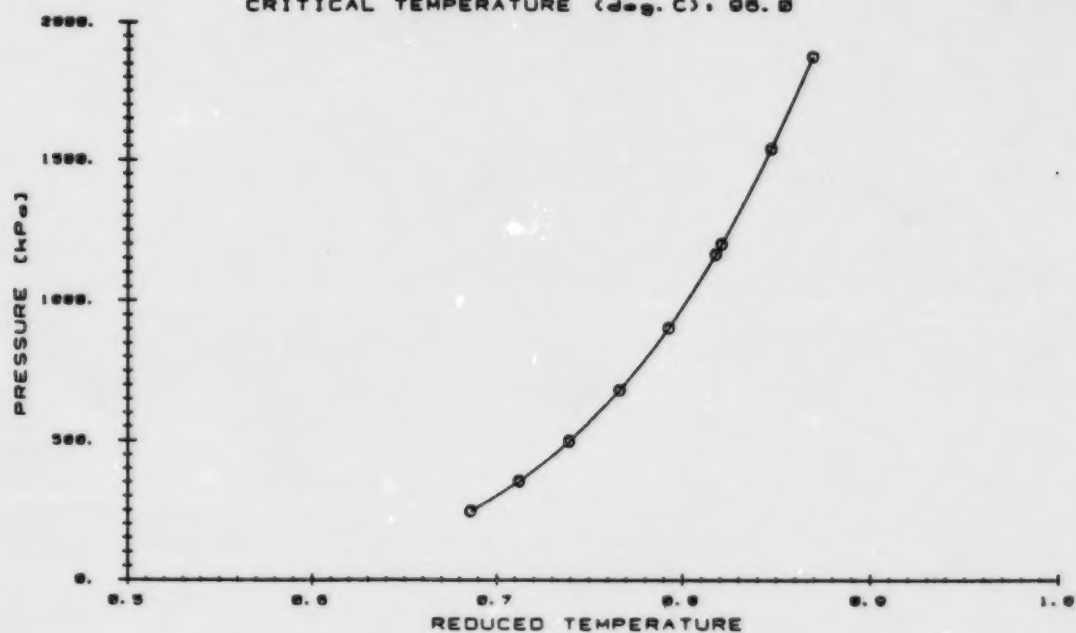


Figure 4 : R-22 experimental results

EXPERIMENTAL RESULTS

REFRIGERANT: R114

CRITICAL TEMPERATURE (deg. C): 145.9

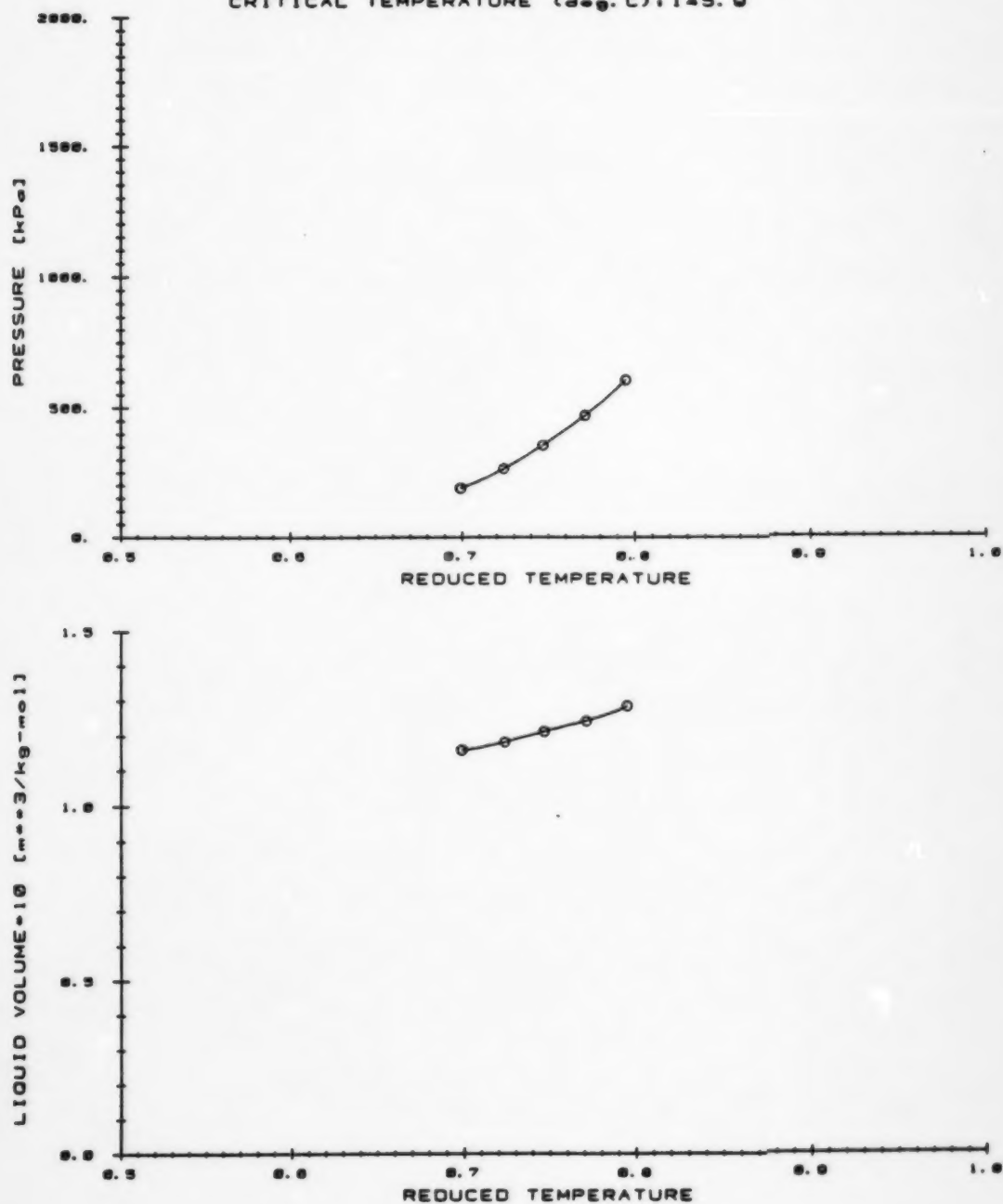


Figure 5 : R-114 experimental results

EXPERIMENTAL RESULTS

REFRIGERANT: R142B

CRITICAL TEMPERATURE (deg. C): 137.1

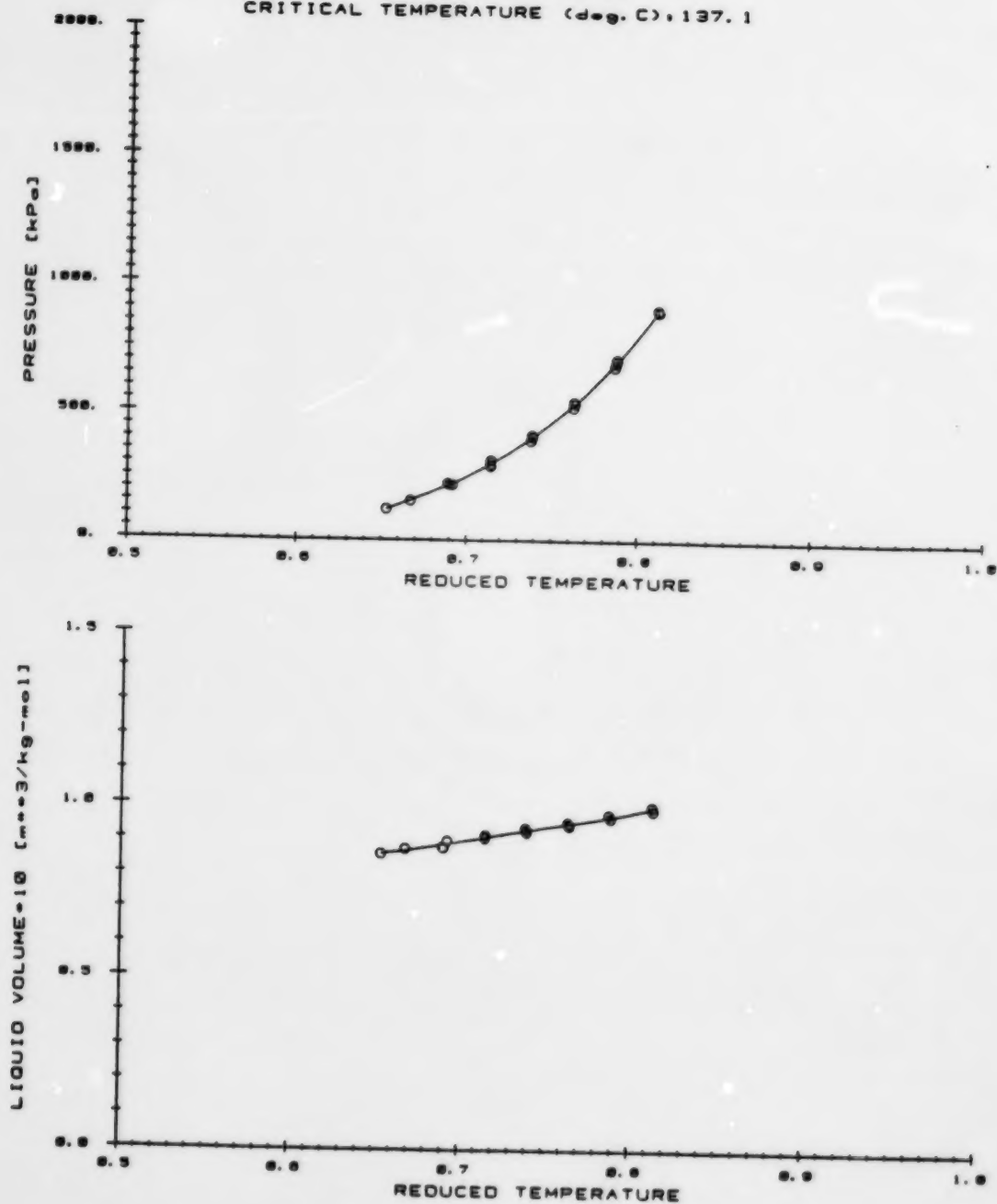


Figure 6 : R-142b experimental results

EXPERIMENTAL RESULTS
REFRIGERANT, R152A
CRITICAL TEMPERATURE (deg. C): 113.5

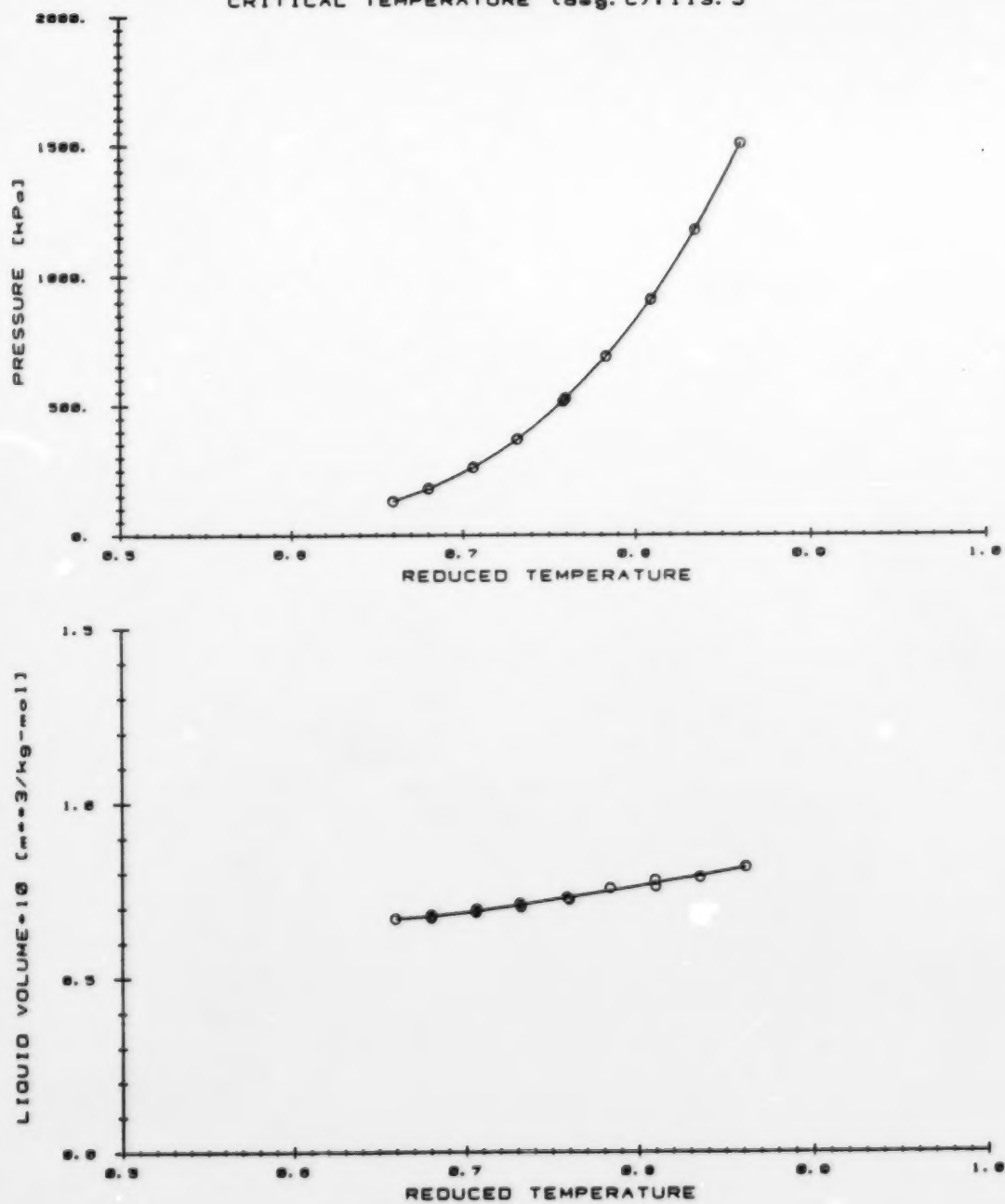


Figure 7 : R-152a experimental results

5.2 REFRIGERANT MIXTURES

The experimental results for the refrigerant mixtures are the same as for the pure ones namely, the saturation pressure P_e , the saturation temperature T_e and the saturated liquid specific volume $V_{l,e}$. The mixture composition X_L is also evaluated in the case of the refrigerant mixtures.

The results of the tests performed on the refrigerant mixtures are presented in Figures 8 through 10 and also in Tables 12-23 at the end of section 6.2. The experimental runs for the mixtures were done in a similar way to those for the pure substances. For each run 7 points were taken in the -20°C to 60°C temperature range. Two runs have only 6 points due to pressure limitations and/or experimental difficulties (R-22/R-142b 69/31, R-22/R-142b 30/70).

None of the mixtures experimentations were repeated mainly due to time limitation and difficulties in obtaining the same sample composition for a second test.

EXPERIMENTAL RESULTS

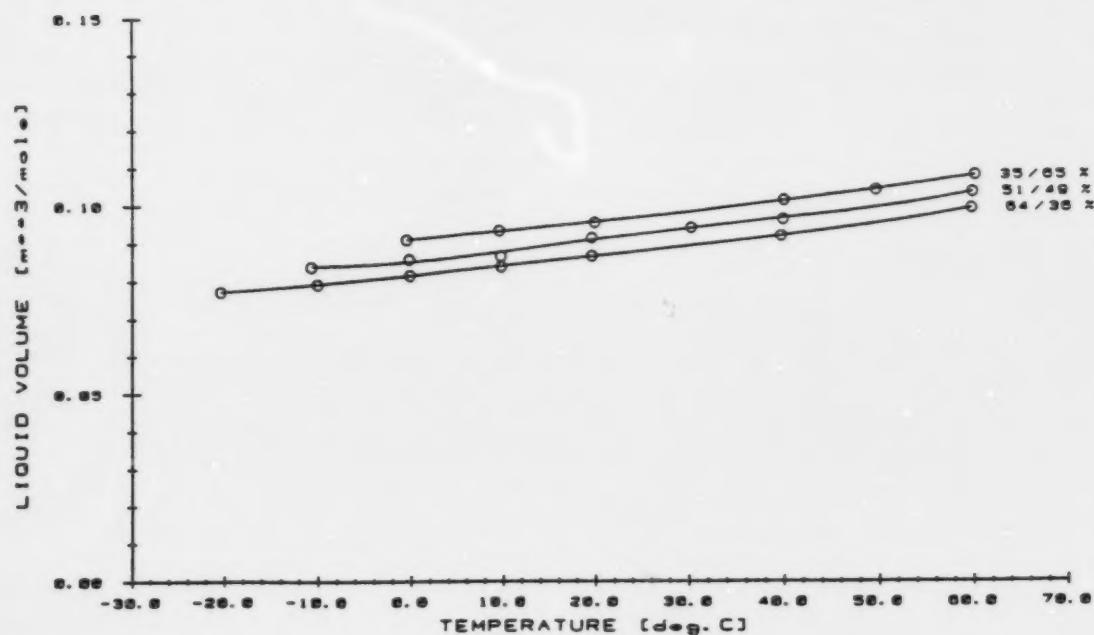
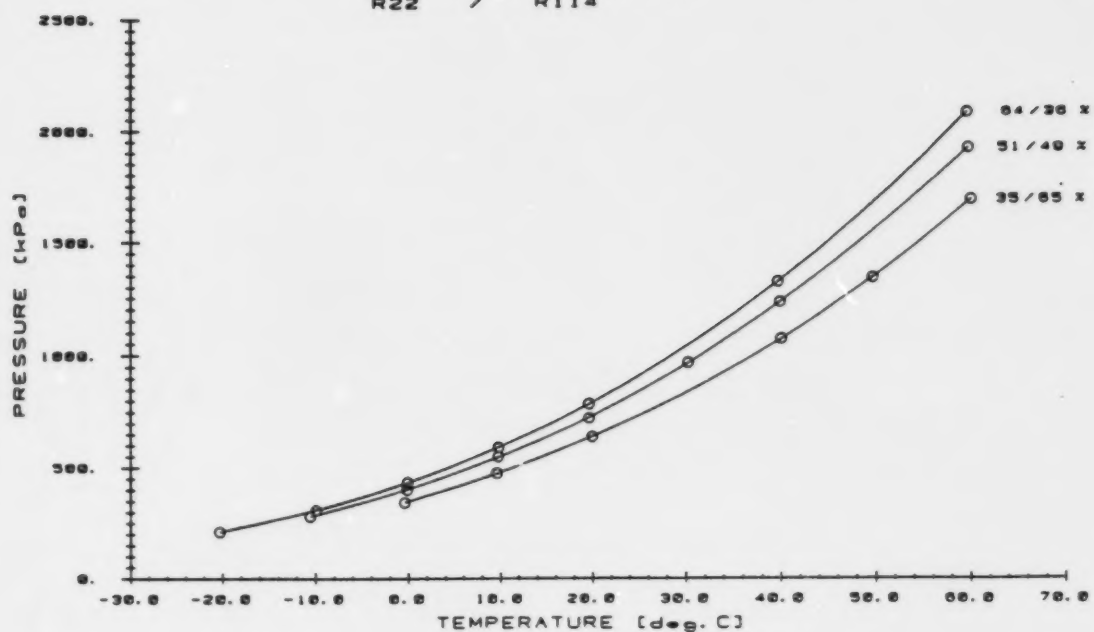
REFRIGERANT MIXTURES
R22 / R114

Figure 8 : R-22/R-114 Experimental results

EXPERIMENTAL RESULTS

REFRIGERANT MIXTURES

R22 / R142B

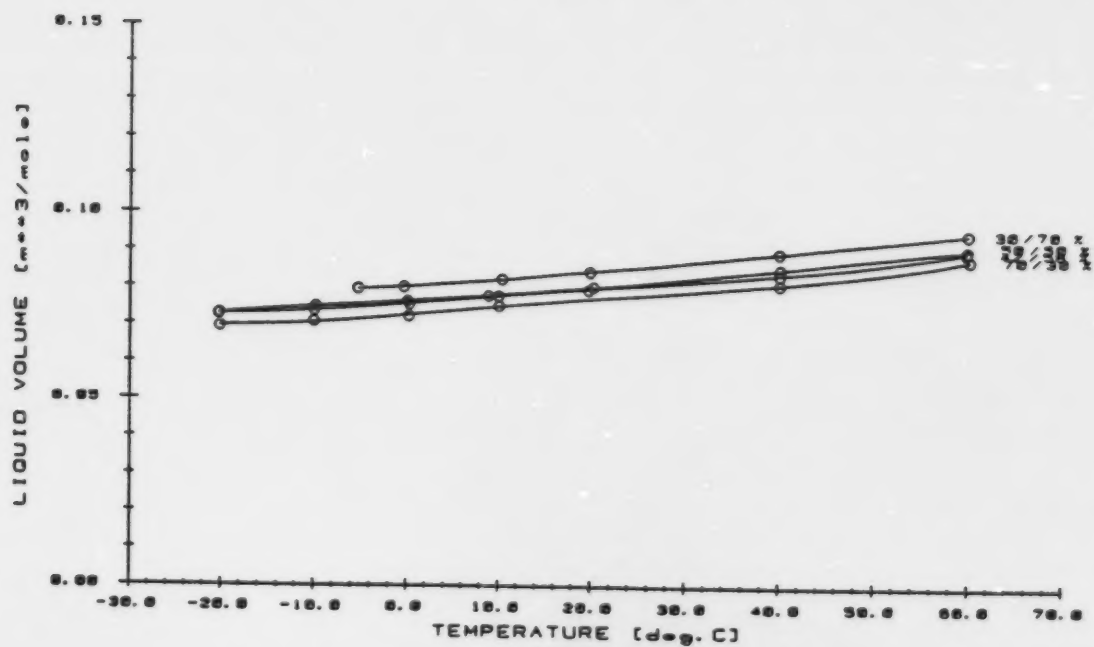
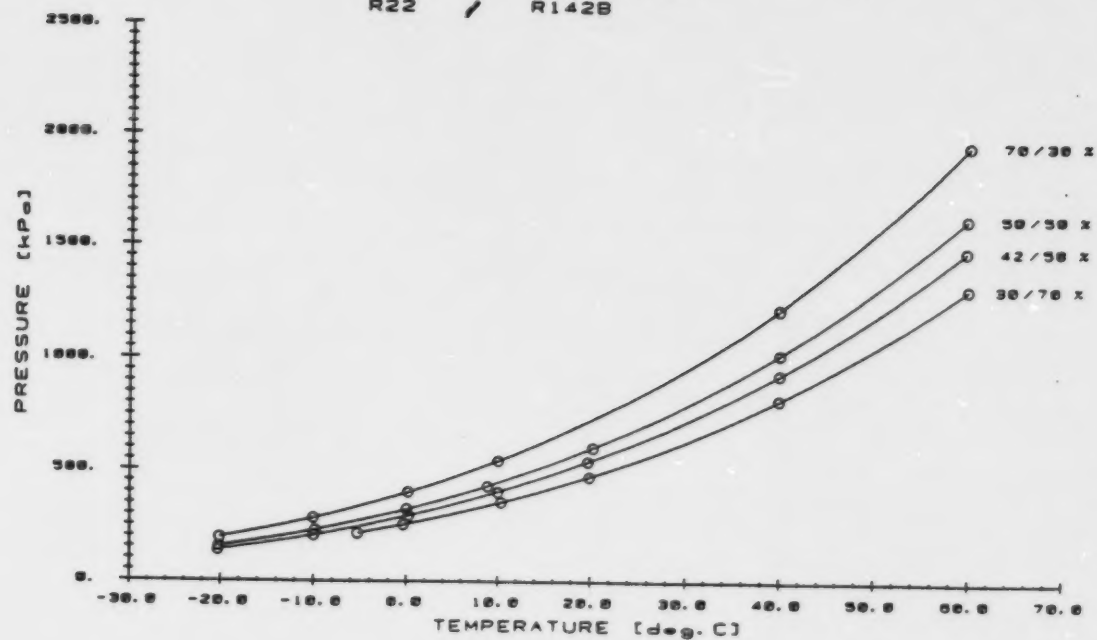


Figure 9 : R-22/R-142b Experimental results

EXPERIMENTAL RESULTS

REFRIGERANT MIXTURES

R22 / R152A

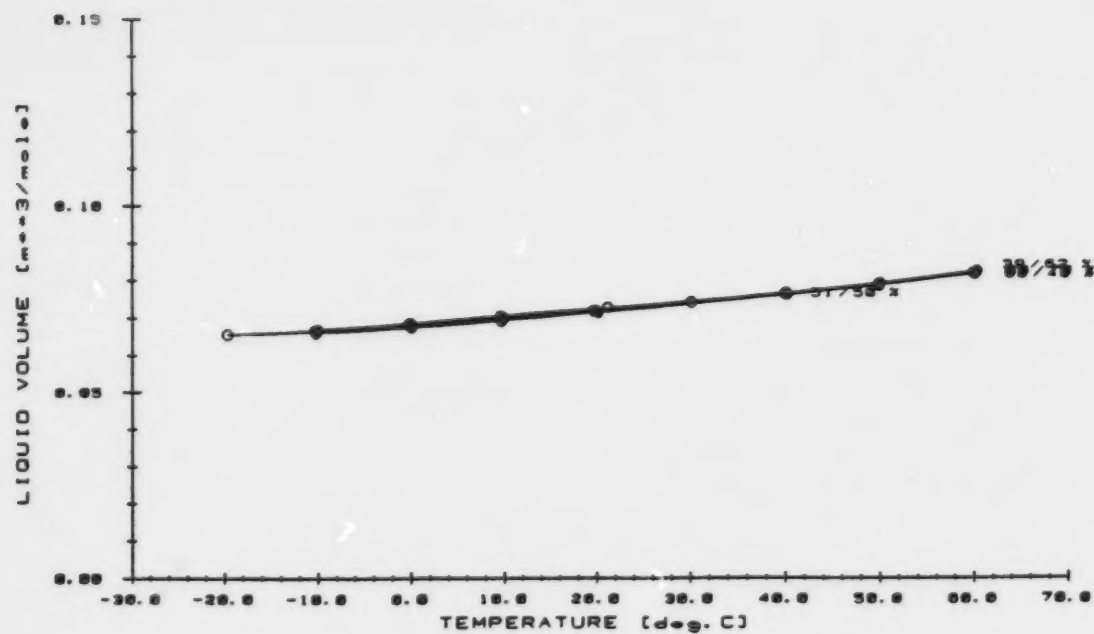
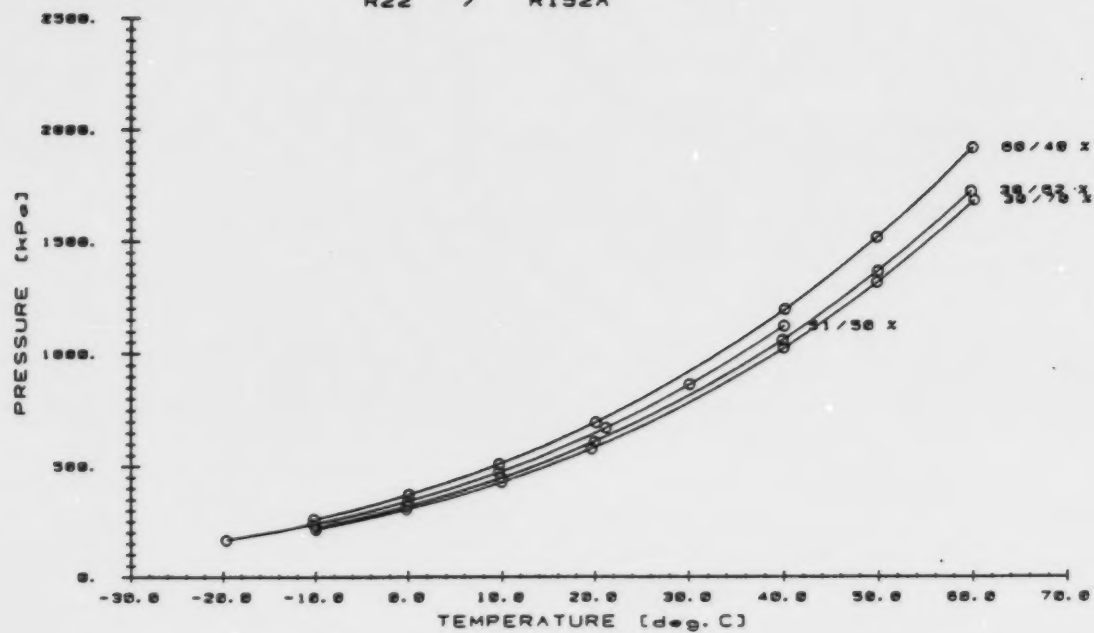


Figure 10 : R-22/R-152a Experimental results

6.0 DATA REDUCTION

The information presented in Section 5.0 enables us to determine the "a" and "b" parameters for the pure substances and the interaction parameter for the mixtures. The process by which these parameters are obtained is described in Section 2.0 of this report.

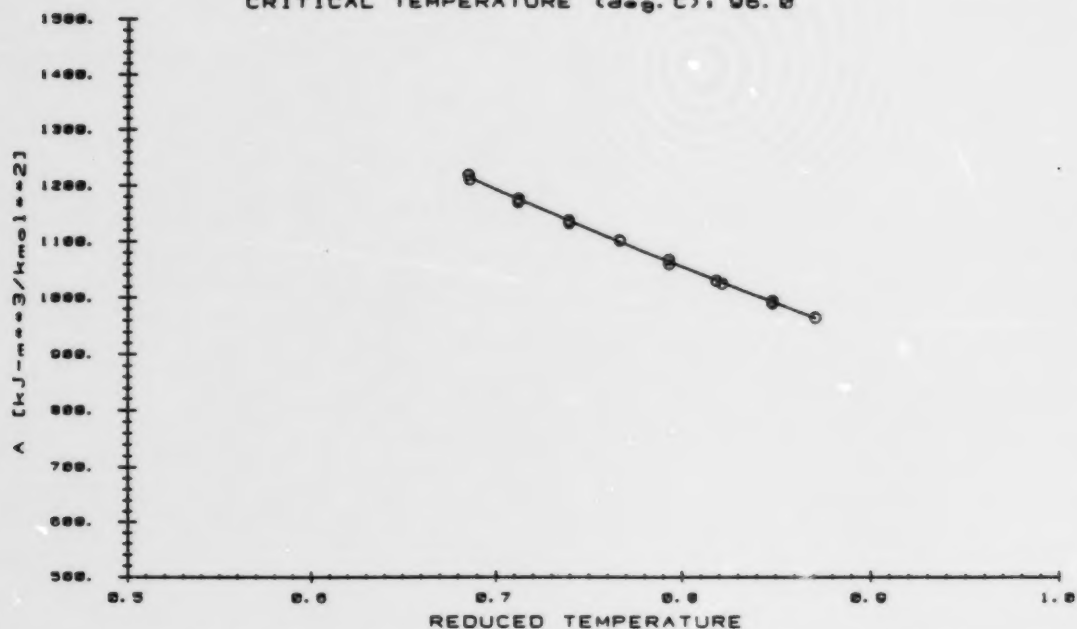
6.1 PURE REFRIGERANTS

The experimental points were used directly along with equation (4) to obtain the "a" and "b" parameters. These results are shown in Figures 11-14 and given in Tables 4-7. Below each graph are the coefficients defined in equations (2) and (3) for the "a" and "b" temperature dependency equations. The tables also contain the saturated pressure P_C and saturated liquid specific volume V_{LC} as computed by the CSD equation of state (using the "a" and "b" values obtained from experimental results). The results shown in Figures 13 and 14 demonstrate some scattering, especially for the "a" parameter. This phenomenon is due to the use of the individual experimental points in equation (4). Therefore, the experimental results were smoothed using a fourth order polynomial, as can be seen on Figures 15-18. Using the polynomial equations obtained from the experimental points, a series of points were selected to calculate the "a" and "b" parameters. These points and the corresponding values of "a" and "b" are shown in Figures 19-22 and given in Tables 8-11 along with the CSD computed values for the saturation pressures and saturated liquid specific volumes. Also shown below each graph are the coefficients needed in equations (2) and (3) to represent the "a" and "b" temperature dependency. There is a noticeable variation in the "a" and "b" values obtained from the smoothed results compared to the one calculated using the experimental points. The smoothed values will be used in equations (5)-(8) to obtain the interaction parameters for the mixtures. This choice was made on the basis that the smoothed experimental points are not as susceptible to experimental bias as are the individual experimental results.

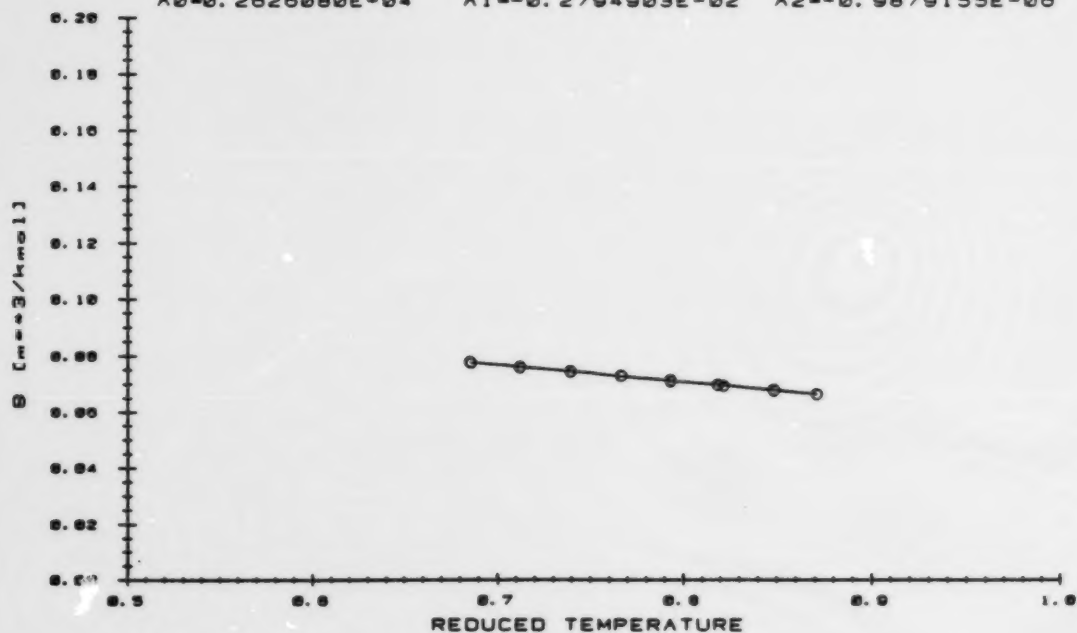
PARAMETERS FOR CSD EQUATION OF STATE

REFRIGERANT: R22

CRITICAL TEMPERATURE (deg. C): 96.0



A0=0.2626080E-04 A1=-0.2794903E-02 A2=-0.9879155E-06



B0=0.1152488E-00 B1=-0.1342457E-03 B2=-0.5315279E-07

Figure 11 : R-22 "a" and "b" parameters

PARAMETERS FOR CSD EQUATION OF STATE

REFRIGERANT, R114

CRITICAL TEMPERATURE (deg. C), 145.9

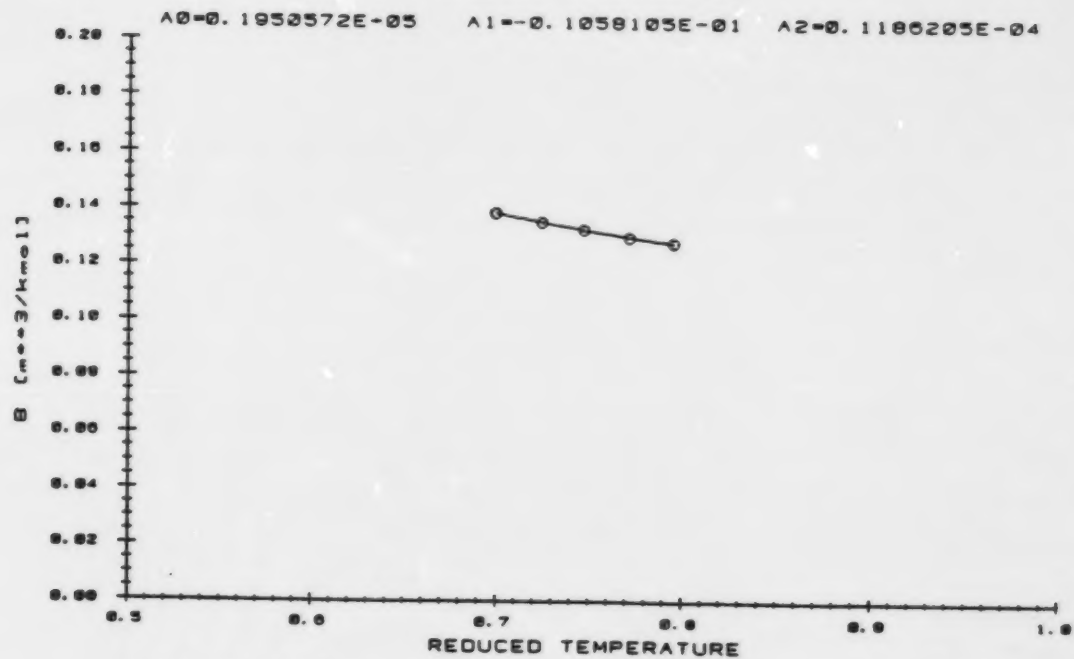
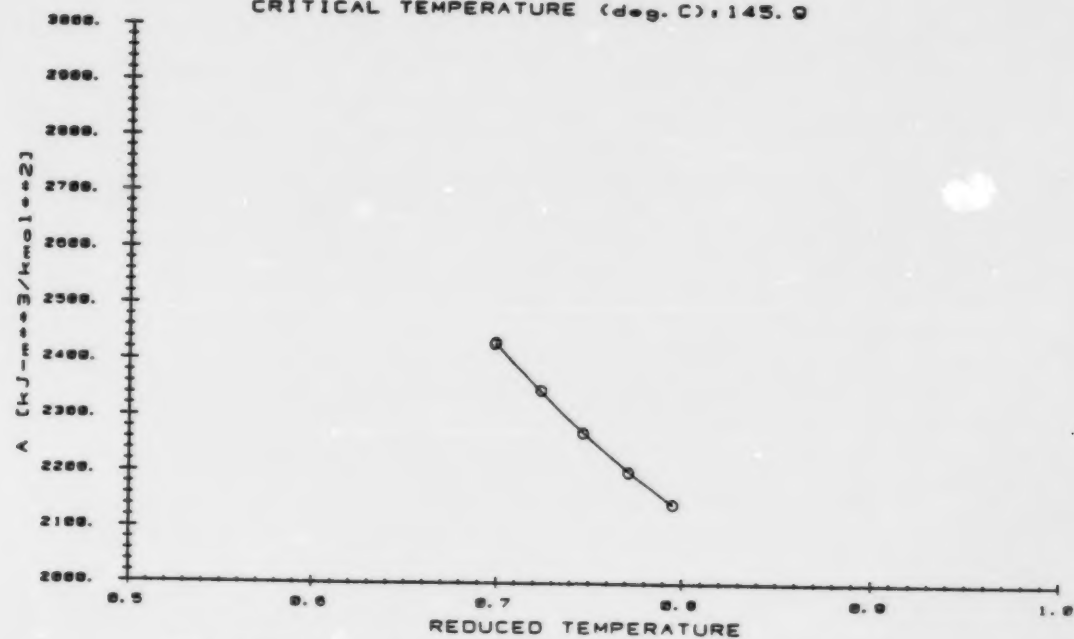
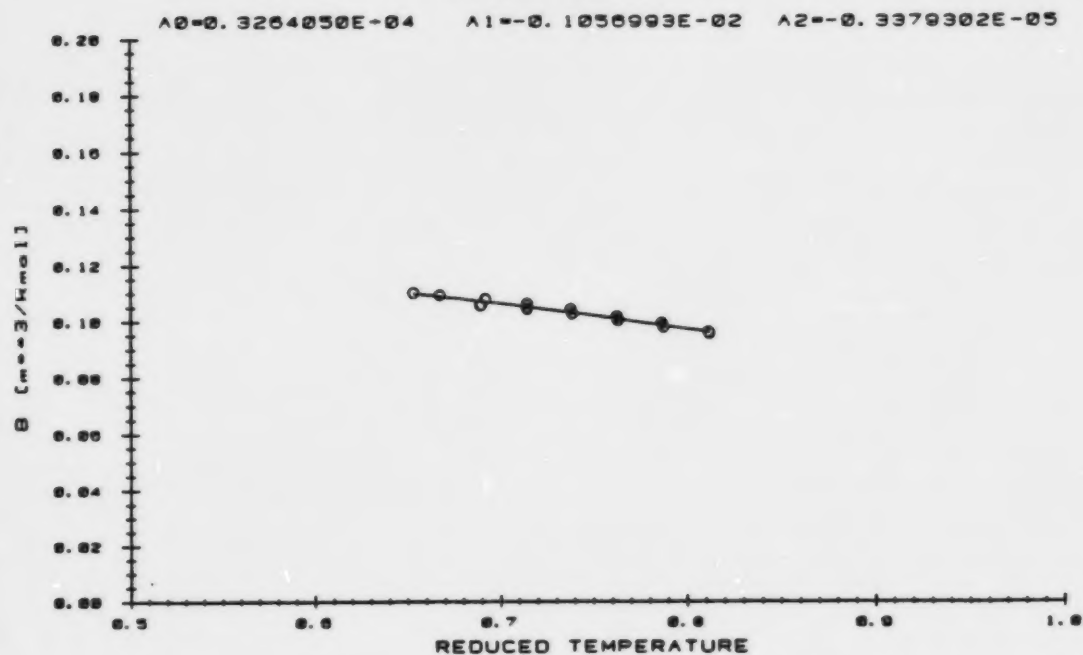
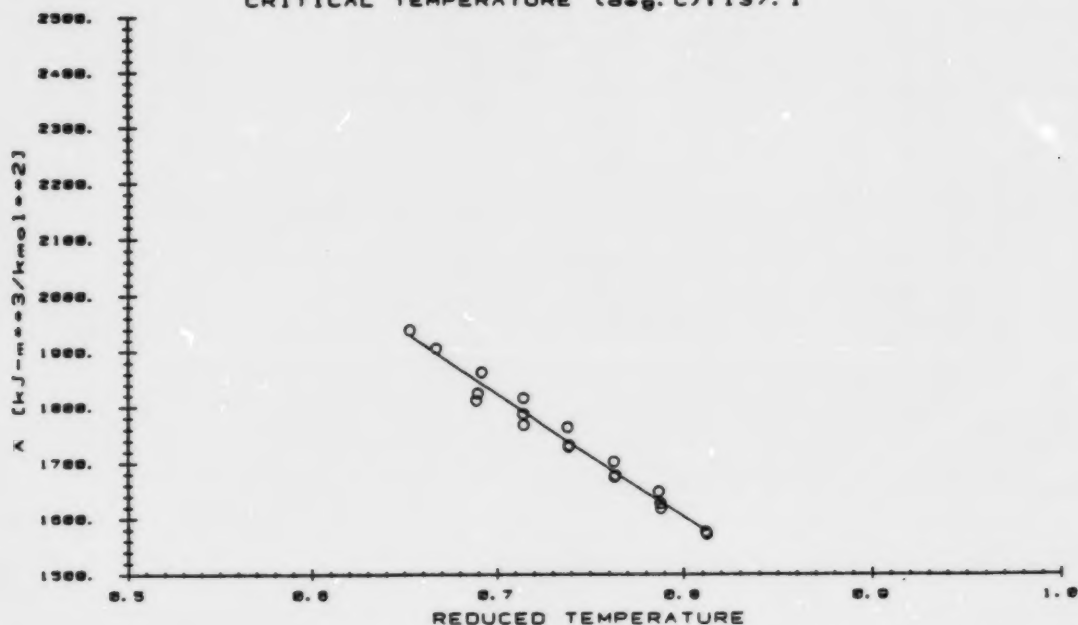


Figure 12 : R-114 "a" and "b" parameters

PARAMETERS FOR CSD EQUATION OF STATE

REFRIGERANT: R142B

CRITICAL TEMPERATURE (deg. C): 137.1



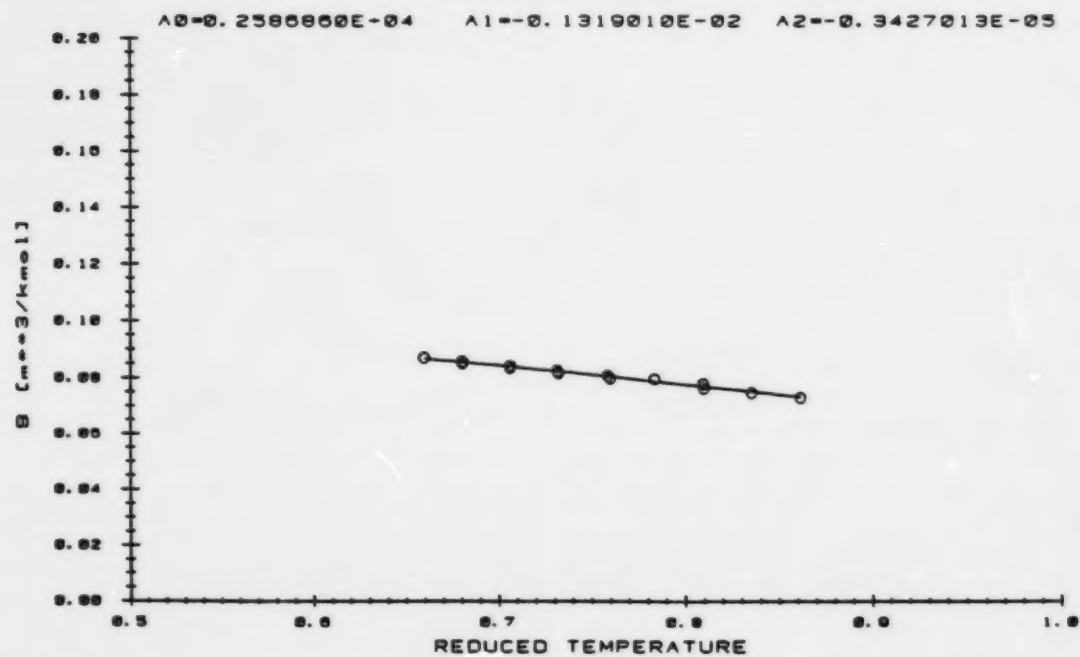
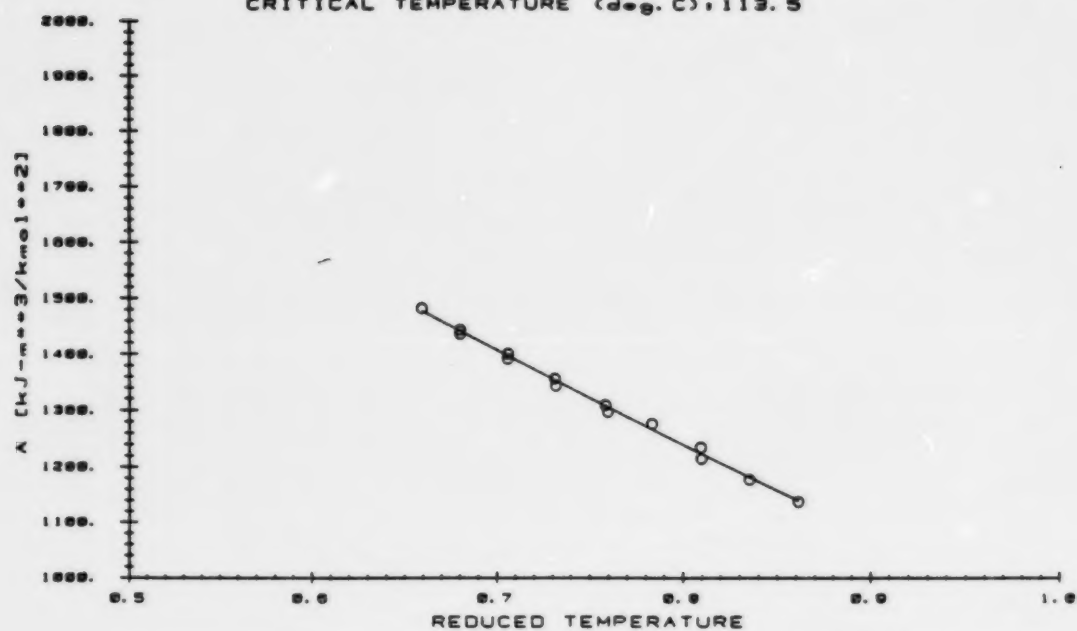
$A0=0.3264050E-04$ $A1=-0.1056993E-02$ $A2=-0.3379302E-05$
 $B0=0.1220624E-00$ $B1=0.8953047E-04$ $B2=-0.5039799E-06$

Figure 13 : R-142b "a" and "b" parameters

PARAMETERS FOR CSD EQUATION OF STATE

REFRIGERANT, R152A

CRITICAL TEMPERATURE (deg. C): 113.5



B0=0.1110686E+00 B1=-0.3595476E-04 B2=-0.2333133E-06

Figure 14 : R-152a "a" and "b" parameters

EXPERIMENTAL RESULTS

PARAMETERS FOR CSD EQUATION OF STATE

REFRIGERANT:R22

T	PE	VLE	A	B	PC	VLC
253.15	244.20	0.06394	0.121965E+04	0.780970E-01	244.20	0.06394
253.32	249.70	0.06381	0.121183E+04	0.777573E-01	249.70	0.06381
263.00	356.70	0.06507	0.117052E+04	0.759510E-01	356.70	0.06507
263.10	352.80	0.06527	0.117726E+04	0.762653E-01	352.80	0.06527
273.09	496.50	0.06704	0.113895E+04	0.746952E-01	496.50	0.06704
273.10	502.30	0.06689	0.113323E+04	0.744240E-01	502.30	0.06689
283.07	682.40	0.06921	0.110269E+04	0.732498E-01	682.40	0.06921
283.11	681.20	0.06905	0.110188E+04	0.731381E-01	681.20	0.06905
292.87	904.80	0.07058	0.106077E+04	0.710788E-01	904.80	0.07058
292.89	903.60	0.07126	0.106796E+04	0.716503E-01	903.60	0.07126
302.17	1164.00	0.07310	0.103076E+04	0.697889E-01	1164.00	0.07310
303.36	1201.00	0.07329	0.102553E+04	0.695034E-01	1201.00	0.07329
313.21	1537.80	0.07648	0.995271E+03	0.681721E-01	1537.80	0.07648
313.29	1540.70	0.07591	0.990541E+03	0.677649E-01	1540.70	0.07591
321.62	1876.00	0.07901	0.965549E+03	0.666263E-01	1876.00	0.07901

Table 4 : R-22 results

EXPERIMENTAL RESULTS

PARAMETERS FOR CSD EQUATION OF STATE

REFRIGERANT:R114

T	PE	VLE	A	B	PC	VLC
292.95	189.41	0.11591	0.242978E+04	0.138218E+00	189.41	0.11591
293.15	189.54	0.11599	0.243265E+04	0.138300E+00	189.54	0.11599
303.44	264.66	0.11829	0.234722E+04	0.135095E+00	264.66	0.11829
313.03	355.88	0.12122	0.227216E+04	0.132475E+00	355.88	0.12122
323.25	470.04	0.12426	0.220108E+04	0.129665E+00	470.04	0.12426
333.18	605.77	0.12858	0.214381E+04	0.127702E+00	605.77	0.12858

Table 5 : R-114 results

PARAMETERS FOR CSD EQUATION OF STATE

REFRIGERANT: R142B

T	PE	VLE	A	B	PC	VLC
268.04	121.50	0.08574	0.193985E+04	0.110162E+00	121.50	0.08574
273.78	154.00	0.08722	0.190615E+04	0.109342E+00	154.00	0.08722
282.74	223.82	0.08775	0.181202E+04	0.105645E+00	223.82	0.08775
283.06	218.65	0.08767	0.182467E+04	0.105879E+00	218.65	0.08767
284.00	217.70	0.08952	0.186282E+04	0.107937E+00	217.70	0.08952
293.15	300.25	0.09035	0.178731E+04	0.104773E+00	300.25	0.09035
293.22	291.20	0.09125	0.181640E+04	0.106125E+00	291.20	0.09125
293.25	314.25	0.09061	0.176851E+04	0.104376E+00	314.25	0.09061
302.92	392.30	0.09335	0.176357E+04	0.104141E+00	392.30	0.09335
303.17	413.00	0.09264	0.172862E+04	0.102663E+00	413.00	0.09264
303.25	406.53	0.09217	0.173163E+04	0.102485E+00	406.53	0.09217
313.05	524.90	0.09523	0.170248E+04	0.101558E+00	524.90	0.09523
313.10	544.57	0.09456	0.167442E+04	0.100335E+00	544.57	0.09456
313.39	540.41	0.09431	0.167766E+04	0.100256E+00	540.41	0.09431
322.84	683.00	0.09754	0.164803E+04	0.992933E-01	683.00	0.09754
323.15	698.32	0.09661	0.162712E+04	0.981219E-01	698.32	0.09661
323.30	710.52	0.09661	0.161824E+04	0.978070E-01	710.52	0.09661
333.10	902.95	0.09986	0.157591E+04	0.961666E-01	902.95	0.09986
333.30	896.03	0.09887	0.157208E+04	0.955894E-01	896.03	0.09887

Table 6 : R-142b results

EXPERIMENTAL RESULTS

PARAMETERS FOR CSD EQUATION OF STATE

REFRIGERANT: R152A

T	PE	VLE	A	B	PC	VLC
255.13	131.30	0.06697	0.148275E+04	0.870833E-01	131.30	0.06697
263.09	178.53	0.06724	0.143729E+04	0.849571E-01	178.53	0.06724
263.12	181.30	0.06803	0.144490E+04	0.857096E-01	181.30	0.06803
273.05	261.71	0.06889	0.139233E+04	0.834535E-01	261.71	0.06889
273.17	263.00	0.06962	0.140210E+04	0.841800E-01	263.00	0.06962
282.90	369.00	0.07114	0.135702E+04	0.824642E-01	369.00	0.07114
283.08	370.86	0.07021	0.134356E+04	0.814896E-01	370.86	0.07021
293.35	516.40	0.07292	0.130969E+04	0.805969E-01	516.40	0.07292
293.95	526.53	0.07232	0.129796E+04	0.798246E-01	526.53	0.07232
303.09	688.00	0.07556	0.127720E+04	0.795843E-01	688.00	0.07556
313.11	908.50	0.07787	0.123538E+04	0.778750E-01	908.50	0.07787
313.23	912.97	0.07602	0.121503E+04	0.763216E-01	912.97	0.07602
323.03	1174.70	0.07860	0.117799E+04	0.747895E-01	1174.70	0.07860
333.15	1506.53	0.08164	0.113812E+04	0.730846E-01	1506.53	0.08164

Table 7 : R-152a results

SMOOTHED EXPERIMENTAL RESULTS

REFRIGERANT, R22

CRITICAL TEMPERATURE (deg. C), 96.0

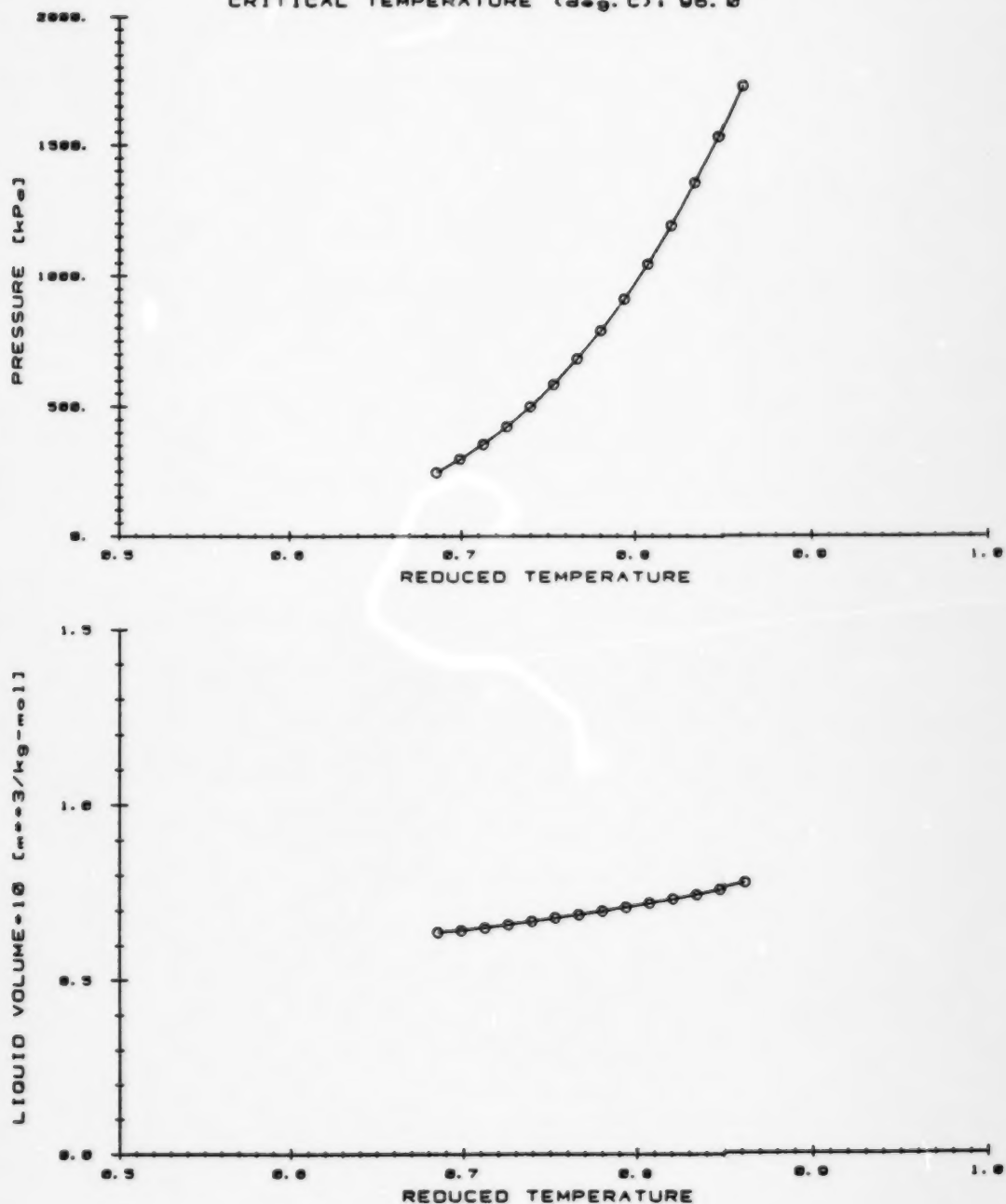


Figure 15 : R-22 smoothed experimental results

SMOOTHED EXPERIMENTAL RESULTS

REFRIGERANT: R114

CRITICAL TEMPERATURE (deg. C): 145.9

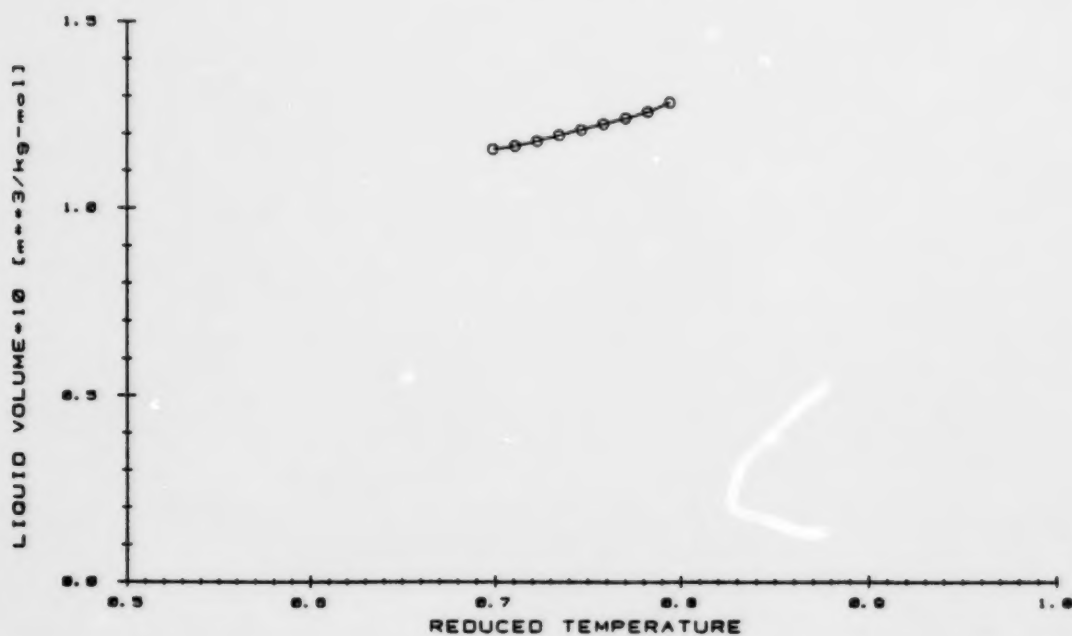
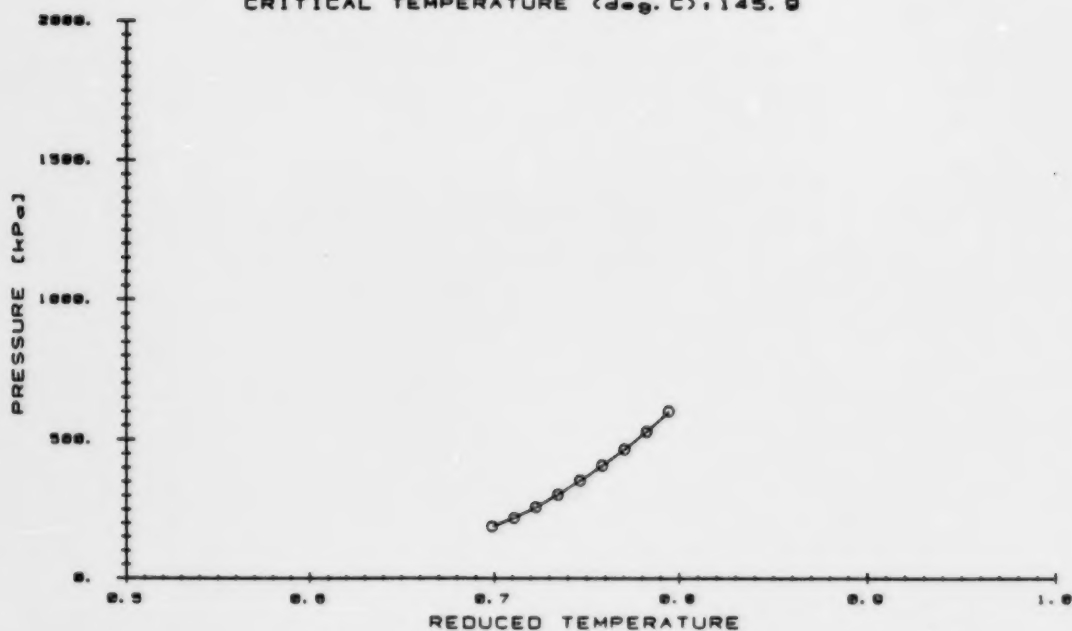


Figure 16 : R-114 smoothed experimental results

SMOOTHED EXPERIMENTAL RESULTS

REFRIGERANT: R142B

CRITICAL TEMPERATURE (deg. C): 137.1

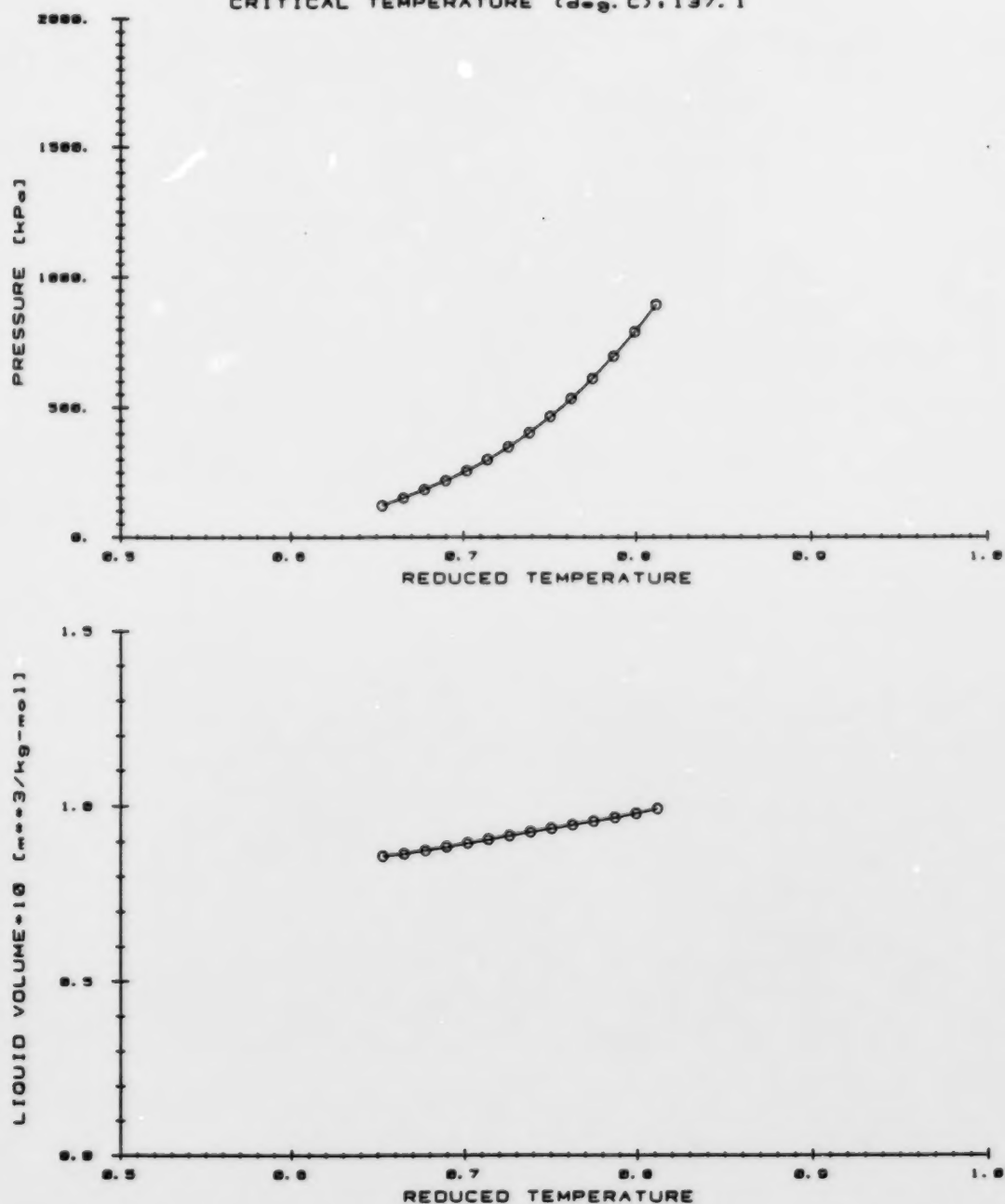


Figure 17 : R-142b smoothed experimental results

SMOOTHED EXPERIMENTAL RESULTS

REFRIGERANT, R152A

CRITICAL TEMPERATURE (deg. C), 113.5

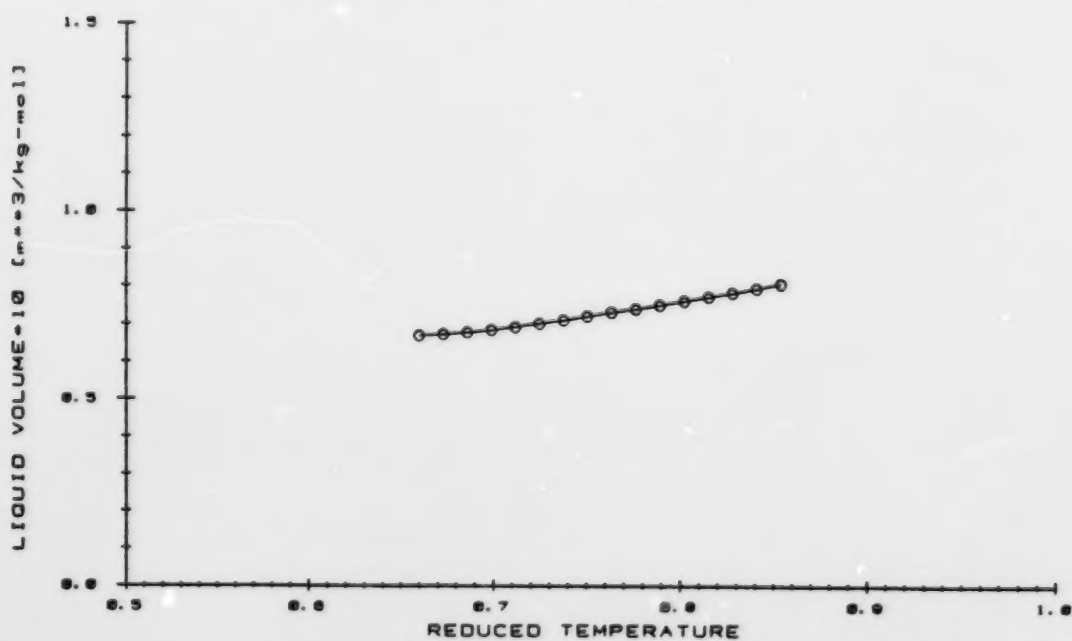
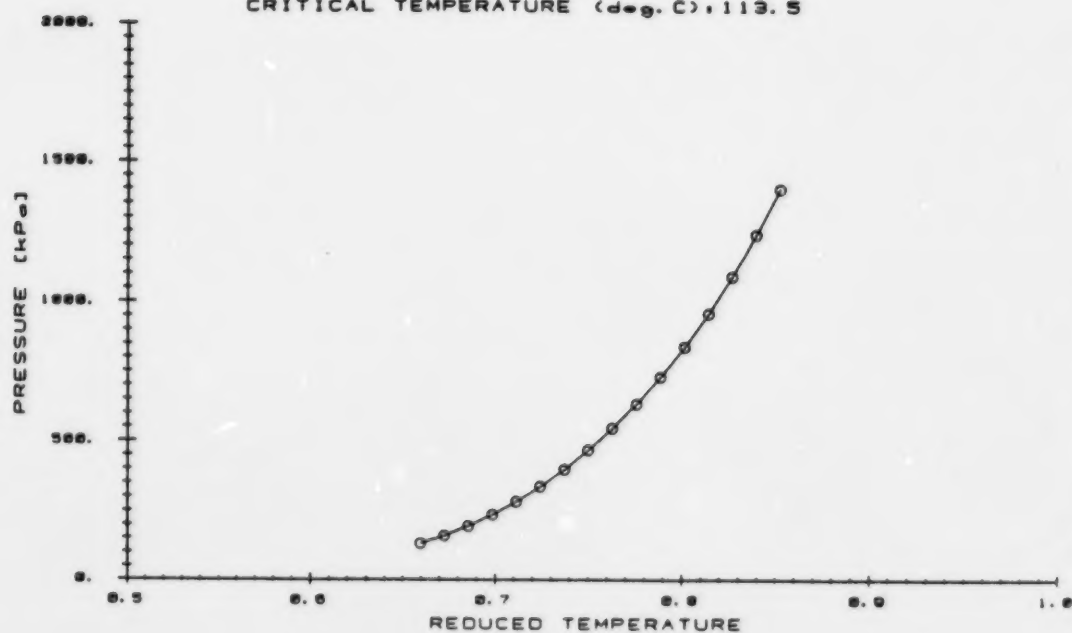


Figure 18 : R-152a smoothed experimental results

PARAMETERS FOR CSD EQUATION OF STATE

REFRIGERANT: R22

CRITICAL TEMPERATURE (deg. C): 96.0

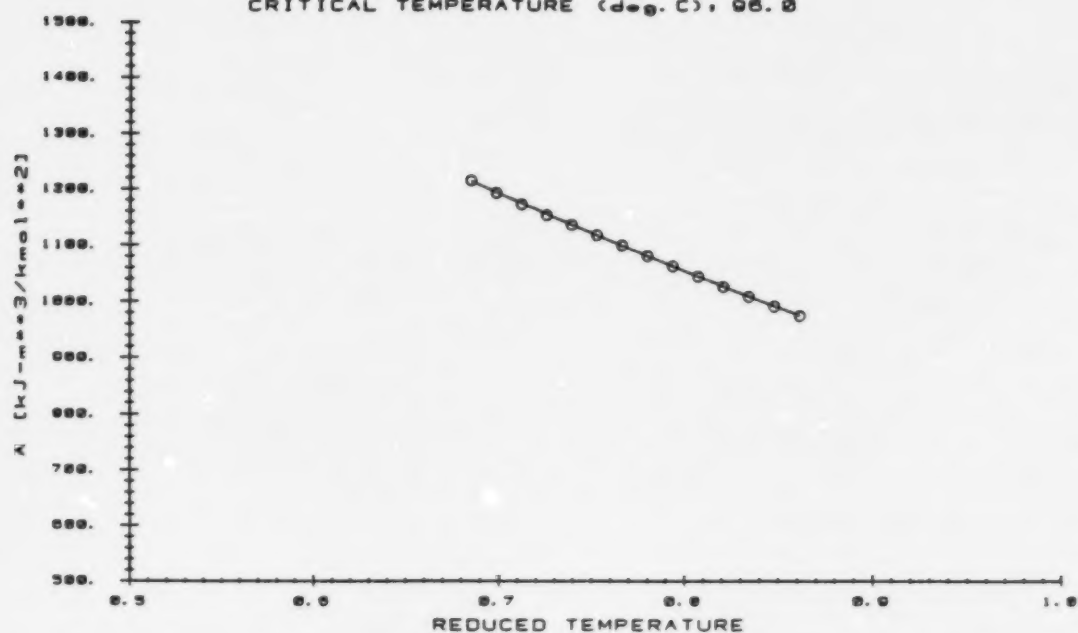
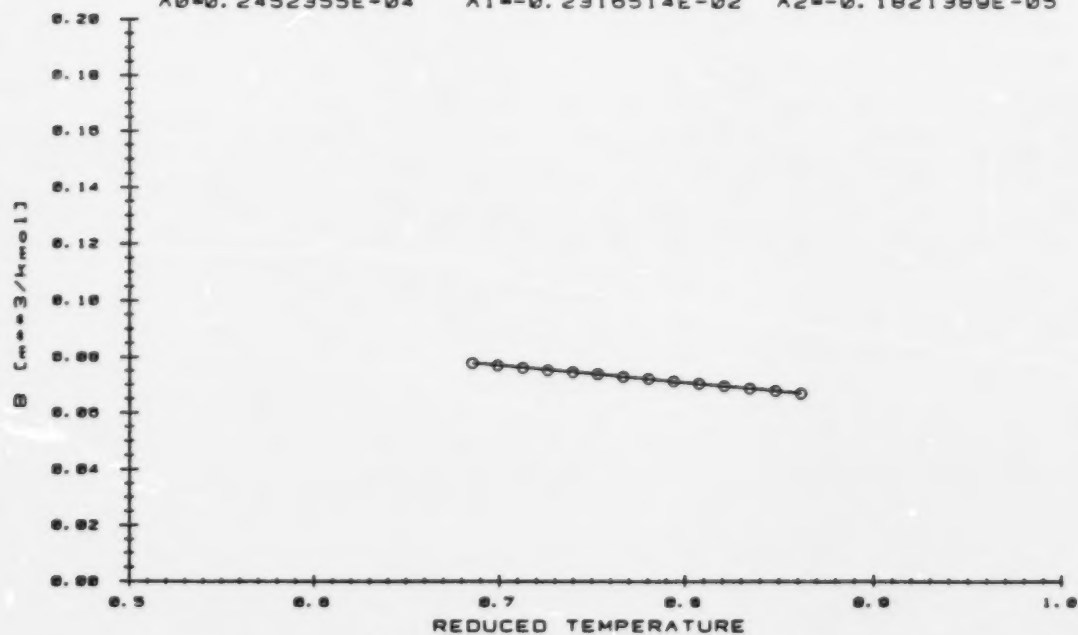
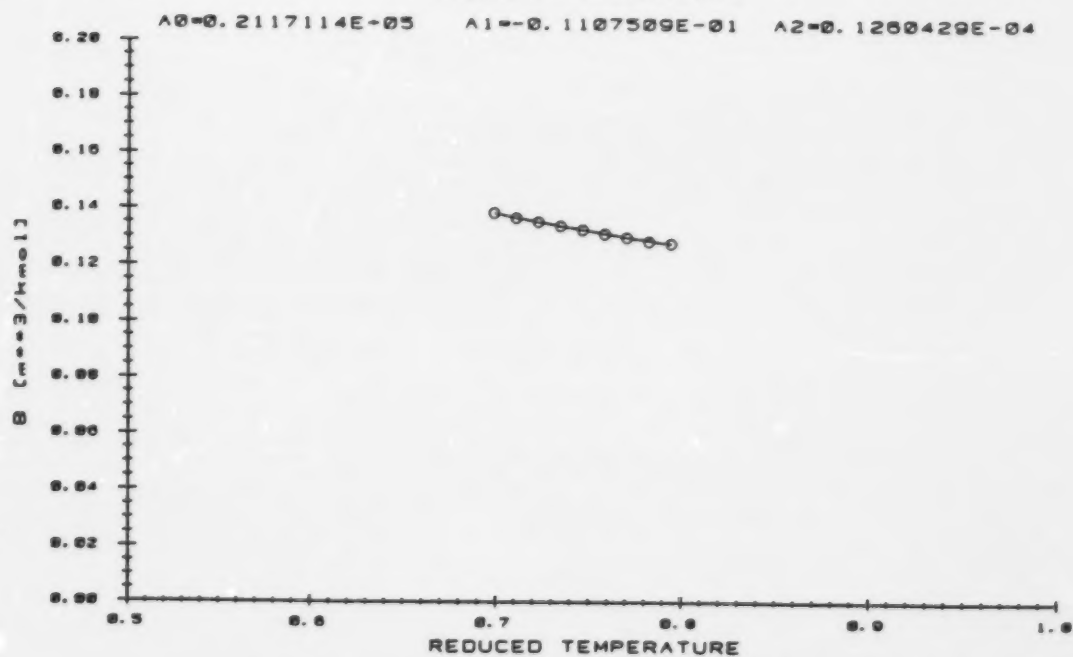
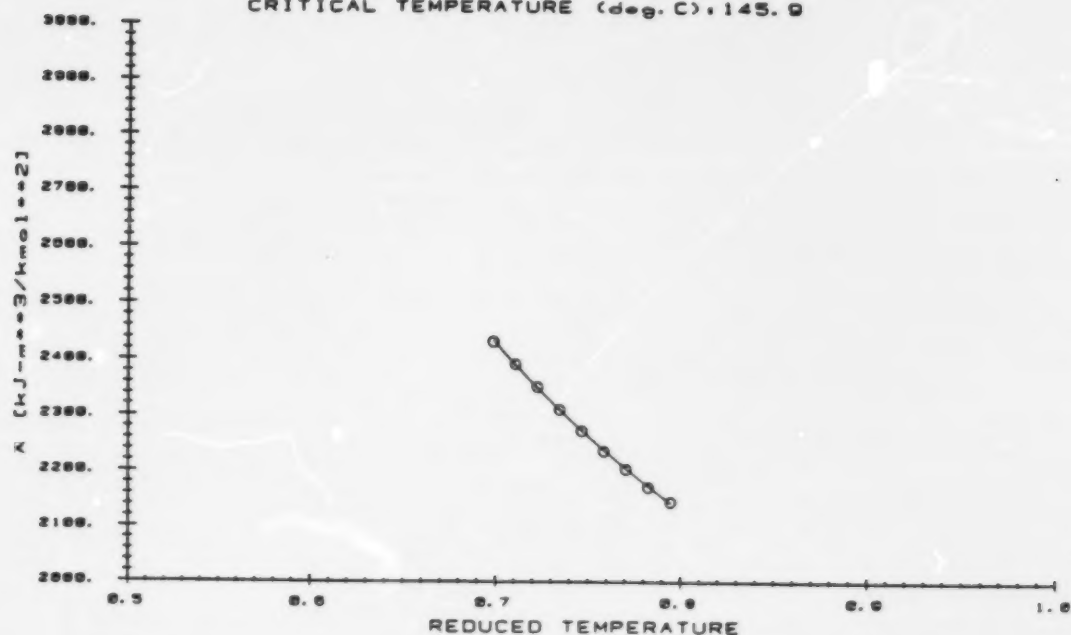

 $A0=0.2452355E-04$ $A1=-0.2316514E-02$ $A2=-0.1621369E-05$

 $B0=0.1095338E+00$ $B1=-0.9421267E-04$ $B2=-0.1230539E-06$

Figure 19 : R-22 smoothed "a" and "b" parameters

PARAMETERS FOR CSD EQUATION OF STATE

REFRIGERANT: R114

CRITICAL TEMPERATURE (deg. C): 145.9



$B0=0.3515251E-00$ $B1=-0.1132426E-02$ $B2=0.1361267E-05$

Figure 20 : R-114 smoothed "a" and "b" parameters

PARAMETERS FOR CSD EQUATION OF STATE

REFRIGERANT: R142B

CRITICAL TEMPERATURE (deg. C): 137.1

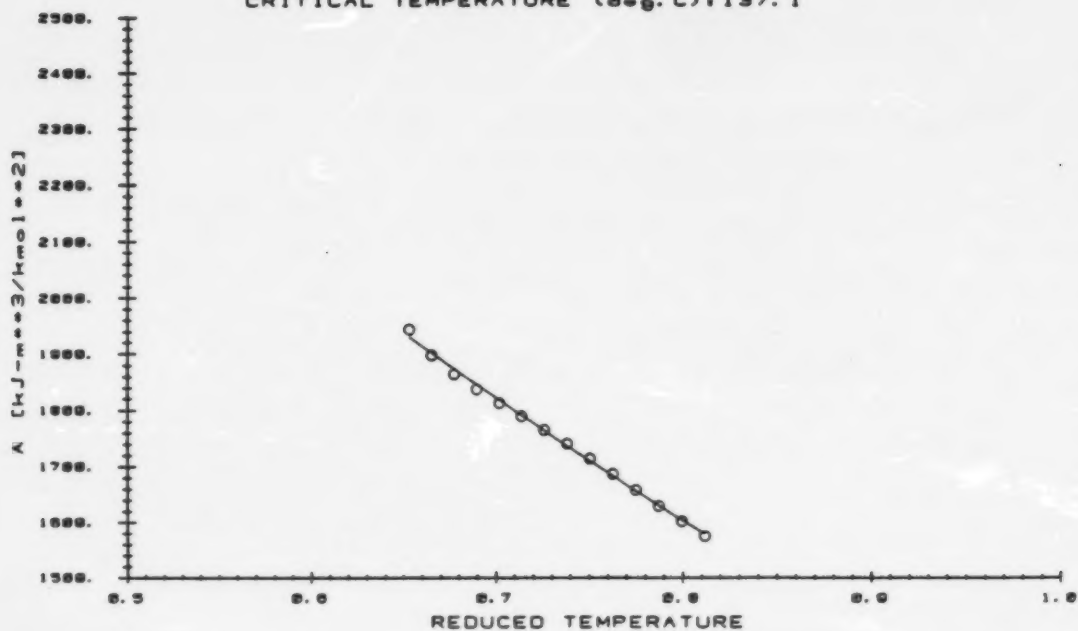
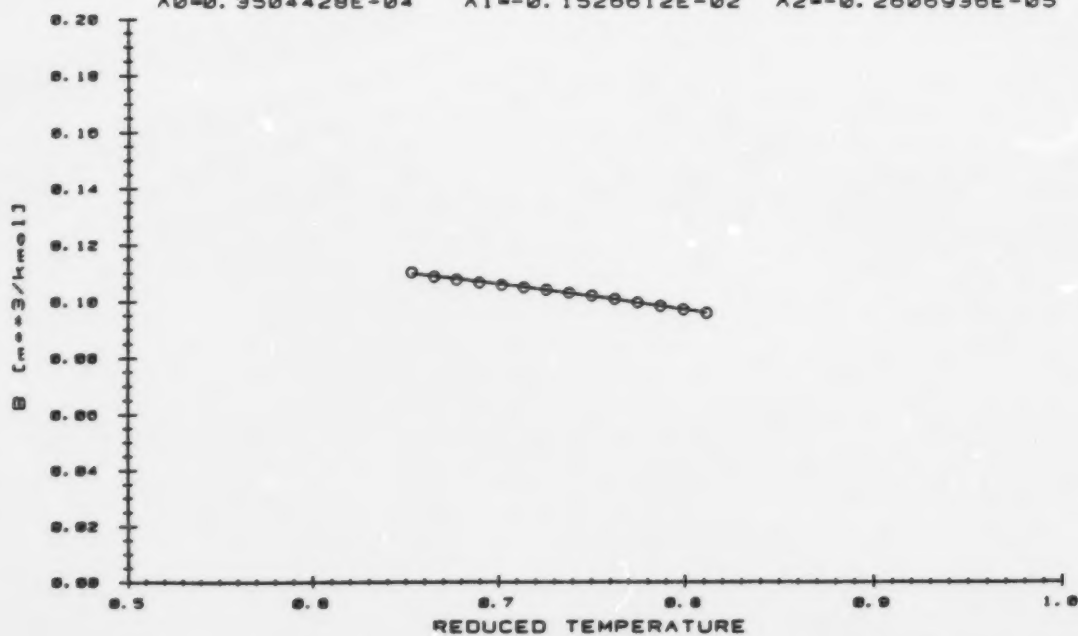

 $A0=0.3504428E-04$ $A1=-0.1526612E-02$ $A2=-0.2606936E-05$

 $B0=0.1256726E+00$ $B1=0.6586237E-04$ $B2=-0.4651893E-06$

Figure 21 : R-142b smoothed "a" and "b"

PARAMETERS FOR CSD EQUATION OF STATE

REFRIGERANT, R152A

CRITICAL TEMPERATURE (deg. C): 113.5

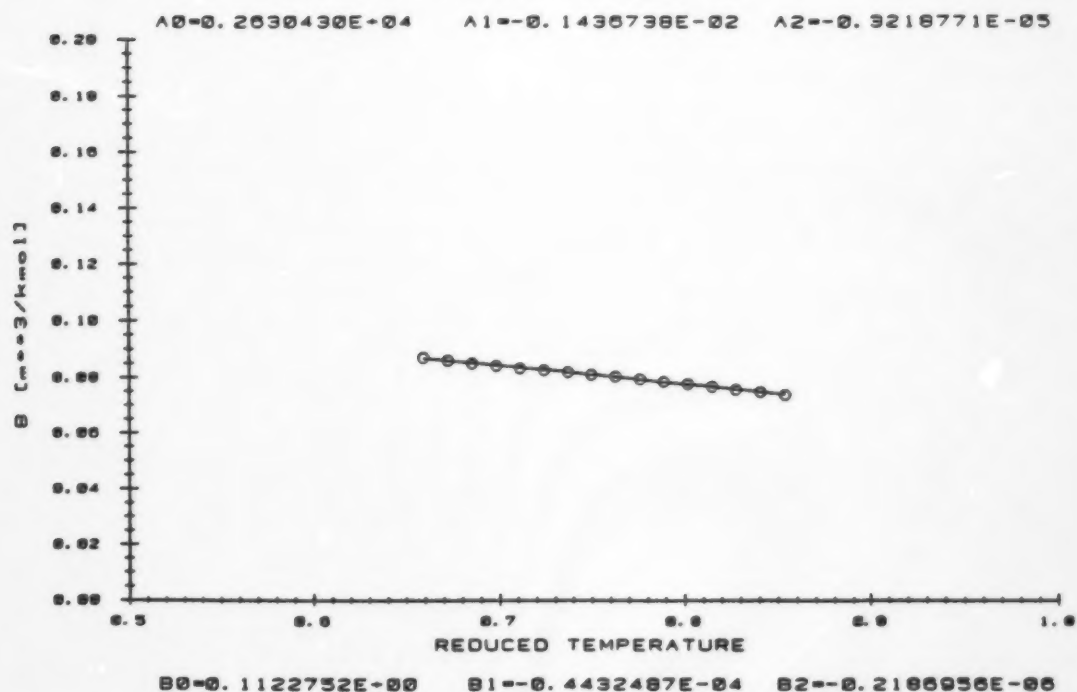
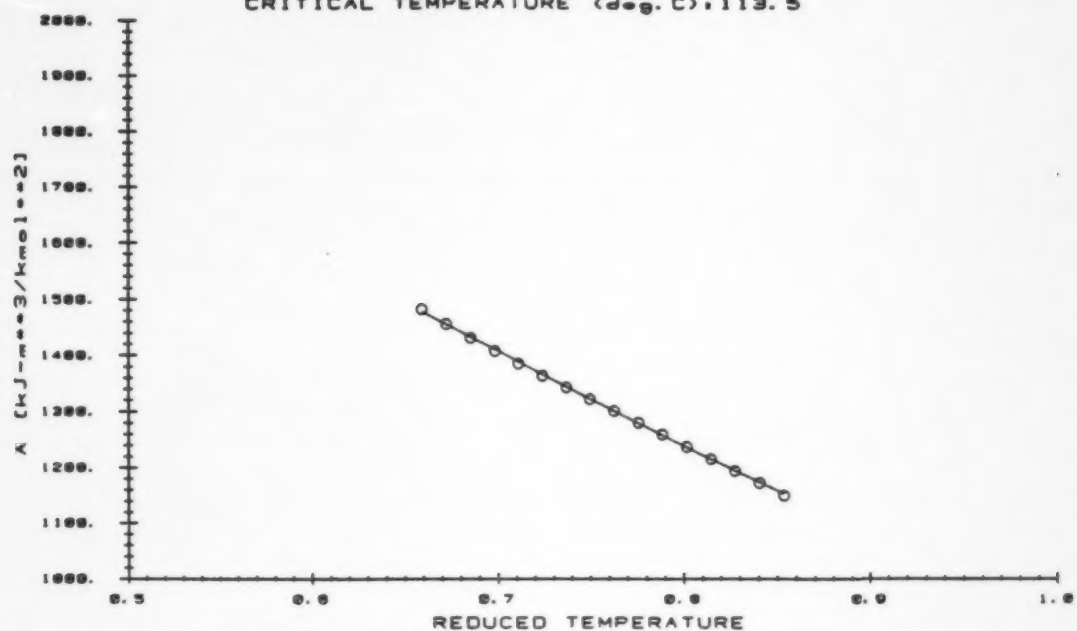


Figure 22 : R-152a smoothed "a" and "b"

SMOOTHED EXPERIMENTAL RESULTS

PARAMETERS FOR CSD EQUATION OF STATE

REFRIGERANT:R22

T	PE	VLE	A	B	PC	VLC
253.15	245.97	0.06386	0.121615E+04	0.779364E-01	245.96	0.06386
258.15	297.58	0.06446	0.119350E+04	0.769492E-01	297.58	0.06446
263.15	356.53	0.06522	0.117341E+04	0.761083E-01	356.53	0.06522
268.15	423.65	0.06608	0.115473E+04	0.753415E-01	423.65	0.06608
273.15	499.83	0.06702	0.113666E+04	0.745985E-01	499.83	0.06702
278.15	585.88	0.06799	0.111876E+04	0.738468E-01	585.88	0.06799
283.15	682.69	0.06899	0.110066E+04	0.730602E-01	682.69	0.06899
288.15	791.05	0.07002	0.108243E+04	0.722420E-01	791.05	0.07002
293.15	911.84	0.07107	0.106399E+04	0.713855E-01	911.84	0.07107
298.15	1045.85	0.07217	0.104557E+04	0.705080E-01	1045.85	0.07217
303.15	1193.92	0.07335	0.102739E+04	0.696262E-01	1193.92	0.07335
308.15	1356.86	0.07463	0.100960E+04	0.687552E-01	1356.86	0.07463
313.15	1535.48	0.07607	0.992560E+03	0.679244E-01	1535.48	0.07607
318.15	1730.58	0.07775	0.976485E+03	0.671552E-01	1730.59	0.07775

Table 8 : R-22 smoothed results

SMOOTHED EXPERIMENTAL RESULTS

PARAMETERS FOR CSD EQUATION OF STATE

REFRIGERANT:R114

T	PE	VLE	A	B	PC	VLC
292.95	188.94	0.11596	0.243224E+04	0.138317E+00	188.94	0.11596
297.95	220.91	0.11679	0.239283E+04	0.136667E+00	220.90	0.11679
302.95	260.31	0.11816	0.235195E+04	0.135263E+00	260.31	0.11816
307.95	305.50	0.11967	0.231111E+04	0.133874E+00	305.50	0.11967
312.95	355.00	0.12117	0.227263E+04	0.132484E+00	355.00	0.12117
317.95	408.75	0.12266	0.223638E+04	0.131094E+00	408.75	0.12266
322.95	466.38	0.12421	0.220353E+04	0.129779E+00	466.37	0.12421
327.95	530.38	0.12598	0.217192E+04	0.128554E+00	530.38	0.12598
332.95	602.00	0.12845	0.214538E+04	0.127748E+00	602.00	0.12845

Table 9 : R-114 smoothed results

PARAMETERS FOR CSD EQUATION OF STATE

REFRIGERANT: R142E

T	PE	VLE	A	B	PC	VLC
268.04	121.00	0.08590	0.194448E+04	0.110392E+00	121.00	0.08590
273.78	155.64	0.08672	0.189300E+04	0.108659E+00	155.64	0.08672
282.74	215.88	0.08840	0.183940E+04	0.106804E+00	215.88	0.08840
283.06	218.23	0.08847	0.183776E+04	0.106746E+00	218.23	0.08847
284.00	225.20	0.08866	0.183309E+04	0.106582E+00	225.20	0.08866
293.15	301.11	0.09061	0.178959E+04	0.104995E+00	301.11	0.09061
293.22	301.75	0.09062	0.178923E+04	0.104981E+00	301.75	0.09062
293.25	302.04	0.09063	0.178912E+04	0.104979E+00	302.04	0.09063
302.92	402.12	0.09268	0.174155E+04	0.103116E+00	402.12	0.09268
303.17	405.02	0.09273	0.174030E+04	0.103066E+00	405.02	0.09273
303.25	405.95	0.09275	0.173989E+04	0.103049E+00	405.95	0.09275
313.05	534.15	0.09476	0.168707E+04	0.100837E+00	534.15	0.09476
313.10	534.87	0.09477	0.168685E+04	0.100828E+00	534.87	0.09477
313.39	539.13	0.09482	0.168515E+04	0.100753E+00	539.14	0.09482
322.84	693.06	0.09681	0.163163E+04	0.984177E-01	693.06	0.09681
323.15	698.67	0.09688	0.162985E+04	0.983393E-01	698.67	0.09688
323.30	701.36	0.09691	0.162898E+04	0.983000E-01	701.36	0.09691
333.10	897.21	0.09934	0.157467E+04	0.959096E-01	897.21	0.09934
333.30	901.59	0.09940	0.157359E+04	0.958612E-01	901.58	0.09940

Table 10 : R-142b smoothed results

SMOOTHED EXPERIMENTAL RESULTS

PARAMETERS FOR CSD EQUATION OF STATE

REFRIGERANT: R152A

T	PE	VLE	A	B	PC	VLC
255.13	131.42	0.06701	0.148312E+04	0.871223E-01	131.42	0.06701
260.13	160.03	0.06735	0.145678E+04	0.859712E-01	160.03	0.06735
265.13	194.47	0.06789	0.143164E+04	0.849744E-01	194.47	0.06789
270.13	235.03	0.06859	0.140794E+04	0.840963E-01	235.03	0.06859
275.13	282.10	0.06940	0.138550E+04	0.832971E-01	282.10	0.06940
280.13	336.10	0.07029	0.136396E+04	0.825389E-01	336.10	0.07029
285.13	397.53	0.07123	0.134302E+04	0.817954E-01	397.53	0.07123
290.13	466.98	0.07221	0.132234E+04	0.810415E-01	466.98	0.07221
295.13	545.06	0.07321	0.130163E+04	0.802565E-01	545.06	0.07321
300.13	632.49	0.07422	0.128076E+04	0.794331E-01	632.49	0.07422
305.13	730.02	0.07523	0.125958E+04	0.785603E-01	730.02	0.07523
310.13	838.50	0.07626	0.123811E+04	0.776422E-01	838.50	0.07626
315.13	958.82	0.07730	0.121637E+04	0.766823E-01	958.81	0.07730
320.13	1091.96	0.07838	0.119438E+04	0.756835E-01	1091.96	0.07838
325.13	1238.94	0.07951	0.117231E+04	0.746593E-01	1238.94	0.07951
330.13	1400.84	0.08071	0.115024E+04	0.736186E-01	1400.84	0.08071

Table 11 : R-152a smoothed results

6.2 REFRIGERANT MIXTURES

The final results to be obtained for the mixtures is the interaction parameter as defined in equation (7). The process by which this parameter is calculated is similar to the one for the "a" and "b" parameters for the pure substances and is described in Section 2.1. Equation (9) is used in the minimization calculations and requires experimental and calculated values. Therefore, the "a" and "b" parameters of the pure substances calculated in section 6.1 are used in determining the interaction parameters of the mixtures. The individual experimental points were employed directly in equation (9) since smoothing of the experimental data did not produce any significant change in the results. This is attributable to the fact that only one series of points were taken for the mixtures compared to 2 or 3 for the pure substances. The calculated interaction parameters are given in Tables 12-22 for the three mixtures tested. In the same tables the CSD computed values of saturation pressure and saturated liquid specific volumes are presented. In the case of the mixtures there is small but noticeable difference between the experimental values and the CSD computed values whereas there is practically no differences in the case of the pure substances.

If we compare the interaction parameters obtained in this work with the one of previous studies [7] it is necessary to take the average of all our points, since the parameters given in [7] are reported as constant with regard to composition and temperature. Table 23 presents the average interaction parameters obtained from the experimental data and the corresponding standard deviations. The interaction parameters reported by McLinden [7] are also given in this table. The standard deviation in the f_{12} values is an indication of the uncertainty arising from scatter in the experimental points and any temperature or composition dependence of f_{12} .

INTERACTION PARAMETER

CSD Equation of State

Refrigerants : R22 --- R114

Composition : 35/65 [% weight] Molecular Weight : 127.00

Experimental Results				Computed Values	
T [deg.K]	PE [kPa]	VLE [m**3/mole]	F [-]	PC [kPa]	VLC [m**3/mole]
272.80	344.69	0.09110	0.0348	343.96	0.09231
282.87	474.84	0.09357	0.0384	474.06	0.09458
293.20	638.05	0.09568	0.0391	636.53	0.09712
313.31	1072.55	0.10170	0.0427	1068.08	0.10355
322.95	1342.18	0.10450	0.0436	1331.49	0.10744
333.38	1690.41	0.10842	0.0463	1668.56	0.11266

Table 12 : R-22/R-114 (35/65) results

Composition : 51/49 [% weight] Molecular Weight : 113.94

Experimental Results				Computed Values	
T [deg.K]	PE [kPa]	VLE [m**3/mole]	F [-]	PC [kPa]	VLC [m**3/mole]
262.60	282.43	0.08398	0.0362	282.78	0.08332
273.06	401.74	0.08593	0.0369	402.28	0.08532
283.03	548.47	0.08677	0.0372	547.53	0.08747
292.90	722.38	0.09170	0.0376	726.60	0.08992
303.52	968.98	0.09443	0.0434	973.16	0.09330
313.20	1232.90	0.09667	0.0432	1233.36	0.09659
333.10	1922.78	0.10394	0.0415	1909.94	0.10533

Table 13 : R-22/R-114 (51/49) results

INTERACTION PARAMETER

CSD Equation of State

Refrigerants : R22 --- R114

Composition : 63/37 [% weight] Molecular Weight : 105.29

Experimental Results				Computed Values	
T [deg.K]	PE [kPa]	VLE [m**3/mole]	F [-]	PC [kPa]	VLC [m**3/mole]
252.88	211.76	0.07746	0.0350	212.34	0.07644
263.26	310.10	0.07941	0.0362	311.31	0.07822
273.13	434.05	0.08179	0.0400	436.51	0.08021
283.06	589.53	0.08404	0.0396	593.66	0.08232
292.90	785.80	0.08687	0.0439	792.66	0.08490
312.99	1323.05	0.09219	0.0444	1330.52	0.09113
333.02	2084.46	0.09963	0.0434	2081.14	0.09990

Table 14 : R-22/R-114 (63/37) results

INTERACTION PARAMETER

CSD Equation of State

Refrigerants : R22 --- R142B

Composition : 30/70 [% weight] Molecular Weight : 95.82

Experimental Results				Computed Values	
T [deg.K]	PE [kPa]	VLE [m**3/mole]	F [-]	PC [kPa]	VLC [m**3/mole]
267.87	211.45	0.07961	-0.0123	211.59	0.07928
272.82	250.88	0.08009	-0.0132	250.78	0.08016
283.53	355.36	0.08211	-0.0144	355.24	0.08216
293.09	471.15	0.08420	-0.0168	471.38	0.08398
313.18	817.55	0.08940	-0.0147	819.37	0.08842
333.19	1314.57	0.09478	-0.0128	1319.27	0.09352

Table 15 : R-22/R-142b (30/70) results

Composition : 41/59 [% weight] Molecular Weight : 94.14

Experimental Results				Computed Values	
T [deg.K]	PE [kPa]	VLE [m**3/mole]	F [-]	PC [kPa]	VLC [m**3/mole]
252.90	136.55	0.07257	-0.0195	136.33	0.07416
263.22	203.63	0.07380	-0.0190	203.14	0.07593
273.40	293.31	0.07553	-0.0173	292.39	0.07779
283.17	402.18	0.07765	-0.0176	400.94	0.07962
292.97	540.45	0.07945	-0.0173	538.29	0.08157
313.25	931.36	0.08363	-0.0178	925.90	0.08601
333.01	1482.12	0.08991	-0.0152	1475.86	0.09128

Table 16 : R-22/R-142b (41/59) results

Composition : 50/50 [% weight] Molecular Weight : 92.89

Experimental Results				Computed Values	
T [deg.K]	PE [kPa]	VLE [m**3/mole]	F [-]	PC [kPa]	VLC [m**3/mole]
253.00	153.46	0.07287	-0.0188	153.61	0.07247
263.35	227.13	0.07483	-0.0190	227.40	0.07419
273.20	321.95	0.07629	-0.0173	322.06	0.07598
282.04	428.04	0.07772	-0.0173	428.19	0.07763
293.48	603.20	0.08012	-0.0164	603.32	0.07995
313.30	1023.47	0.08510	-0.0140	1025.54	0.08452
333.10	1625.74	0.09054	-0.0108	1628.65	0.09009

Table 17 : R-22/R-142b (50/50) results

Composition : 69/31 [% weight] Molecular Weight : 90.28

Experimental Results				Computed Values	
T [deg.K]	PE [kPa]	VLE [m**3/mole]	F [-]	PC [kPa]	VLC [m**3/mole]
253.05	191.70	0.06939	-0.0135	191.90	0.06902
263.12	280.82	0.07073	-0.0106	280.80	0.07075
273.35	397.94	0.07222	-0.0118	397.51	0.07251
283.20	542.46	0.07493	-0.0104	543.45	0.07442
313.22	1222.46	0.08098	-0.0132	1221.84	0.08107
333.39	1955.48	0.08784	-0.0044	1958.18	0.08763

Table 18 : R-22/R-142b (69/31) results

INTERACTION PARAMETER

CSD Equation of State

Refrigerants : R22 --- R152A

Composition : 29/71 [% weight] Molecular Weight : 71.08

Experimental Results				Computed Values	
T [deg.K]	PE [kPa]	VLE [m**3/mole]	F [-]	PC [kPa]	VLC [m**3/mole]
263.22	214.50	0.06669	-0.0142	214.38	0.06688
272.99	305.00	0.06818	-0.0154	304.85	0.06835
283.18	429.80	0.06988	-0.0152	429.59	0.07002
292.90	580.30	0.07168	-0.0161	580.08	0.07173
313.25	1026.20	0.07620	-0.0149	1027.52	0.07597
323.13	1317.90	0.07889	-0.0135	1321.91	0.07844
333.50	1684.40	0.08223	-0.0116	1694.66	0.08144

Table 19 : R-22/R-152a (29/71) results

Composition : 38/62 [% weight] Molecular Weight : 72.62

Experimental Results				Computed Values	
T [deg.K]	PE [kPa]	VLE [m**3/mole]	F [-]	PC [kPa]	VLC [m**3/mole]
263.14	225.60	0.06663	-0.0140	225.59	0.06662
273.03	320.84	0.06782	-0.0156	320.52	0.06810
283.10	448.30	0.06955	-0.0159	447.92	0.06975
293.20	610.60	0.07170	-0.0164	610.83	0.07155
313.13	1063.00	0.07625	-0.0144	1065.89	0.07577
323.20	1368.40	0.07901	-0.0130	1375.30	0.07834
333.08	1725.80	0.08170	-0.0130	1733.62	0.08116

Table 20 : R-22/R-152a (38/62) results

Composition : 50/50 [% weight] Molecular Weight : 74.99

Experimental Results				Computed Values	
T [deg.K]	PE [kPa]	VLE [m**3/mole]	F [-]	PC [kPa]	VLC [m**3/mole]
253.55	167.00	0.06551	-0.0171	167.36	0.06481
262.90	238.80	0.06650	-0.0185	239.12	0.06612
273.12	342.90	0.06840	-0.0188	343.99	0.06768
282.85	472.50	0.07021	-0.0183	474.56	0.06930
294.41	671.80	0.07263	-0.0171	676.23	0.07145
303.38	865.30	0.07411	-0.0173	869.96	0.07325
313.27	1124.90	0.07648	-0.0161	1132.54	0.07551

Table 21 : R-22/R-152a (50/50) results

Composition : 60/40 [% weight] Molecular Weight : 77.02

Experimental Results				Computed Values	
T [deg.K]	PE [kPa]	VLE [m**3/mole]	F [-]	PC [kPa]	VLC [m**3/mole]
263.00	261.00	0.06600	-0.0142	261.10	0.06598
273.22	371.90	0.06744	-0.0164	371.64	0.06751
282.93	509.90	0.06897	-0.0164	509.47	0.06915
293.38	697.77	0.07126	-0.0159	698.54	0.07110
313.41	1197.89	0.07615	-0.0142	1204.07	0.07553
323.13	1519.29	0.07835	-0.0149	1523.71	0.07803
333.31	1918.50	0.08156	-0.0142	1926.56	0.08115

Table 22 : R-22/R-152a (60/40) results

MIXTURE	Interaction parameter f_{12}	
	CRIQ	McLINDEN
R-22/R-114	$f_{12} = 0,04$ $\sigma = 0,003$	$f_{12} = 0.03$
R-22/R-142b	$f_{12} = -0,015$ $\sigma = 0,003$	$f_{12} = -0.01$
R-22/R-152a	$f_{12} = -0,016$ $\sigma = 0,002$	$f_{12} = -0.014$

Table 23 : Interaction parameter f_{12} σ : Standard deviation

7.0 DISCUSSION

The work done throughout this study was aimed at determining the interaction parameter f_{12} , as defined in the CSD equation of state, for three refrigerant mixtures. There is a difference between the actual values of f_{12} we obtained and the ones provided by McLinden [7]. However, given the standard deviation calculated for our interaction parameter, and assuming a similar one for McLinden's, it is safe to say that those results are in agreement within experimental uncertainty.

In order to demonstrate the effects of experimental errors on the value of the interaction parameter a sensitivity analysis was carried out. A specific mixture was chosen as a nominal case and a series of tests were simulated on the computer. In each test a different experimental variable was changed by $\pm 1\%$. Table 24 summarizes the cases treated in the sensitivity analysis.

NOMINAL CASE	R-22 / R-152a (50/50)	
SATURATION PRESSURE	$P_{sat} + 1\% P_{sat}$	$P_{sat} - 1\% P_{sat}$
SPECIFIC VOLUME	$V_L + 1\% V_L$	$V_L - 1\% V_L$
COMPOSITION	$X_L + 1\% X_L$	$X_L - 1\% X_L$

Table 24 : Sensitivity analysis

The results of the sensitivity analysis are presented in Tables 26-32. At the bottom of each table the average value of f_{12} is given along with its standard deviation.

The reference point for this sensitivity analysis is a R-22 / R-152a mixture of 50/50 composition. This nominal case is composed of a series of 9 points obtained from the CSD equation of state in which the interaction parameter is set to $F_{12} = -0.014$ and the "a" and "b" parameters are computed using ASHRAE data for pure substances [8]. This reference case is presented in Table 26.

The first set of results, Tables 27-28, is for a variation in the saturation pressure of $+1\%$ and -1% , keeping the temperature and specific volume constant. The effect on the interaction parameter is very strong; in the first case the average parameter is $f_{12} = -0.0106$ and in the second case $f_{12} = -0.0175$ yielding an overall average of $f_{12} = -0.014$. Therefore, a change of $\pm 1\%$ in the saturation pressure leads to a $\pm 25\%$ change in the interaction parameter.

The second set of results, Tables 29-30, is for a change in composition of + 1% and - 1% while keeping all other experimental parameters constant. The specific volume specified in m^3/mole takes on different values in Tables 29 and 30 due only to the change in molecular weight of the mixture. A + 1% change in the mixture composition brought the interaction parameter to $f_{12} = -0.0122$ whereas a - 1% change took it to $f_{12} = -0.0158$. The overall average is $f_{12} = -0.014$ with a $\pm 13\%$ variation for a $\pm 1\%$ change in composition.

The last set of results, Tables 31-32, is for a + 1% and - 1% change in the saturated liquid specific volume while keeping the pressure and composition constant. The resulting variation in the interaction parameter for a $\pm 1\%$ change in V_L is not as strong as those seen in the two previous cases. The parameter varied from $f_{12} = -0.0132$ to $f_{12} = -0.0147$ with an average of $f_{12} = -0.014$, $\pm 5\%$ for a $\pm 1\%$ change in V_L . A summary of the sensitivity analysis results is presented in Table 25.

	+ 1%	- 1%	AVERAGE	% Change in f_{12}
P_e	$f_{12} = -0.0106$ $\sigma = 0.004$	$f_{12} = -0.0175$ $\sigma = 0.0004$	$f_{12} = -0.014$	$\pm 25\%$
X_e	$f_{12} = -0.0122$ $\sigma = 0.0002$	$f_{12} = -0.0158$ $\sigma = 0.0002$	$f_{12} = -0.014$	$\pm 13\%$
V_e	$f_{12} = -0.0132$ $\sigma = 0.0004$	$f_{12} = -0.0147$ $\sigma = 0.0004$	$f_{12} = -0.014$	$\pm 5\%$

Table 25 : Sensitivity analysis results nominal case
R-22/R-152a (50/50) $f_{12} = -0.014$

INTERACTION PARAMETER

CSD Equation of State

Refrigerants : R22 --- R152A

Composition : 50/50 [% weight] Molecular Weight : 74.89

Experimental Results				Computed Values	
T [deg.K]	PE [kPa]	VLE [m**3/mole]	F [-]	PC [kPa]	VLC [m**3/mole]
253.15	168.00	0.06483	-0.0140	168.02	0.06484
263.15	246.16	0.06625	-0.0140	246.19	0.06625
273.15	350.01	0.06779	-0.0140	350.05	0.06779
283.15	484.74	0.06948	-0.0140	484.80	0.06948
293.15	655.96	0.07135	-0.0140	656.04	0.07135
303.15	869.65	0.07346	-0.0140	869.75	0.07346
313.15	1132.15	0.07585	-0.0140	1132.28	0.07586
323.15	1450.17	0.07862	-0.0140	1450.33	0.07863
333.15	1830.77	0.08189	-0.0140	1830.92	0.08189

Table 26 : Sensitivity analysis, nominal case.

CSD Equation of State

Refrigerants : R22 --- R152A

Composition : 50/50 [% weight] Molecular Weight : 74.89

Experimental Results				Computed Values	
T [deg.K]	PE [kPa]	VLE [m**3/mole]	F [-]	PC [kPa]	VLC [m**3/mole]
253.15	169.68	0.06483	-0.0113	169.60	0.06490
263.15	248.62	0.06625	-0.0111	248.55	0.06633
273.15	353.51	0.06779	-0.0108	353.45	0.06788
283.15	489.59	0.06948	-0.0106	489.56	0.06959
293.15	662.51	0.07135	-0.0106	662.09	0.07148
303.15	878.34	0.07346	-0.0104	877.85	0.07361
313.15	1143.47	0.07585	-0.0101	1142.92	0.07604
323.15	1464.67	0.07862	-0.0101	1463.24	0.07884
333.15	1849.07	0.08189	-0.0101	1846.38	0.08215

$$(f_{12})_{ave.} = -0.0106 \quad \sigma = 0.004$$

Table 27 : Sensitivity analysis results, $PE = PE_{nominal} + 1\% PE_{nominal}$

Composition : 50/50 [% weight] Molecular Weight : 74.89

Experimental Results				Computed Values	
T [deg.K]	PE [kPa]	VLE [m**3/mole]	F [-]	PC [kPa]	VLC [m**3/mole]
253.15	166.32	0.06483	-0.0168	166.32	0.06477
263.15	243.70	0.06625	-0.0171	243.66	0.06617
273.15	346.51	0.06779	-0.0171	346.69	0.06770
283.15	479.89	0.06948	-0.0173	480.09	0.06937
293.15	649.40	0.07135	-0.0176	649.61	0.07122
303.15	860.95	0.07346	-0.0178	861.18	0.07330
313.15	1120.83	0.07585	-0.0178	1121.74	0.07567
323.15	1435.67	0.07862	-0.0180	1436.75	0.07840
333.15	1812.46	0.08189	-0.0180	1814.64	0.08163

$$(f_{12})_{ave.} = -0.0175 \quad \sigma = 0.0004$$

Table 28 : Sensitivity analysis results, $PE = PE_{nominal} - 1\% PE_{nominal}$

CSD Equation of State

Refrigerants : R22 --- R152A

Composition : 49/51 [% weight] Molecular Weight : 74.69

Experimental Results				Computed Values	
T [deg.K]	PE [kPa]	VLE [m**3/mole]	F [-]	PC [kPa]	VLC [m**3/mole]
253.15	168.00	0.06466	-0.0120	168.01	0.06490
263.15	246.16	0.06607	-0.0120	246.13	0.06632
273.15	350.01	0.06760	-0.0120	349.93	0.06786
283.15	484.74	0.06929	-0.0120	484.59	0.06956
293.15	655.96	0.07116	-0.0123	655.29	0.07143
303.15	869.65	0.07326	-0.0123	868.77	0.07354
313.15	1132.15	0.07565	-0.0123	1131.04	0.07595
323.15	1450.17	0.07841	-0.0123	1448.82	0.07873
333.15	1830.77	0.08167	-0.0125	1828.17	0.08199

$$(f_{12})_{ave.} = -0.0122 \quad \sigma = 0.0002$$

Table 29 : Sensitivity analysis results, $XE = XE_{nominal} + 1\% XE_{nominal}$

Composition : 51/49 [% weight] Molecular Weight : 75.09

Experimental Results				Computed Values	
T [deg.K]	PE [kPa]	VLE [m**3/mole]	F [-]	PC [kPa]	VLC [m**3/mole]
253.15	168.00	0.06501	-0.0159	168.06	0.06477
263.15	246.16	0.06643	-0.0159	246.28	0.06618
273.15	350.01	0.06797	-0.0159	350.21	0.06771
283.15	484.74	0.06966	-0.0159	485.05	0.06940
293.15	655.96	0.07154	-0.0159	656.39	0.07127
303.15	869.65	0.07365	-0.0159	870.23	0.07337
313.15	1132.15	0.07606	-0.0156	1133.56	0.07576
323.15	1450.17	0.07883	-0.0156	1451.89	0.07853
333.15	1830.77	0.08211	-0.0154	1833.74	0.08180

$$(f_{12})_{ave.} = -0.0158 \quad \sigma = 0.0002$$

Table 30 : Sensitivity analysis results, $XE = XE_{nominal} - 1\% XE_{nominal}$

CSD Equation of State

Refrigerants : R22 --- R152A

Composition : 50/50 [% weight] Molecular Weight : 74.89

Experimental Results				Computed Values	
T [deg.K]	PE [kPa]	VLE [m**3/mole]	F [-]	PC [kPa]	VLC [m**3/mole]
253.15	168.00	0.06548	-0.0137	168.17	0.06484
263.15	246.16	0.06691	-0.0137	246.39	0.06626
273.15	350.01	0.06846	-0.0135	350.57	0.06780
283.15	484.74	0.07017	-0.0135	485.48	0.06949
293.15	655.96	0.07206	-0.0132	657.33	0.07138
303.15	869.65	0.07419	-0.0132	871.36	0.07349
313.15	1132.15	0.07661	-0.0130	1134.93	0.07590
323.15	1450.17	0.07940	-0.0128	1454.35	0.07869
333.15	1830.77	0.08270	-0.0125	1836.70	0.08199

 $(F_{12})_{ave.} = -0.0132$ $\sigma = 0.0004$ Table 31 : Sensitivity analysis results, $VLE = VLE_{nominal} + 1\% VLE_{nominal}$

Composition : 50/50 [% weight] Molecular Weight : 74.89

Experimental Results				Computed Values	
T [deg.K]	PE [kPa]	VLE [m**3/mole]	F [-]	PC [kPa]	VLC [m**3/mole]
253.15	168.00	0.06418	-0.0142	167.88	0.06483
263.15	246.16	0.06558	-0.0144	245.80	0.06624
273.15	350.01	0.06710	-0.0144	349.53	0.06777
283.15	484.74	0.06878	-0.0144	484.12	0.06946
293.15	655.96	0.07063	-0.0147	654.74	0.07133
303.15	869.65	0.07271	-0.0149	867.60	0.07342
313.15	1132.15	0.07509	-0.0149	1129.63	0.07581
323.15	1450.17	0.07784	-0.0152	1446.32	0.07856
333.15	1830.77	0.08106	-0.0154	1825.16	0.08180

 $(f_{12})_{ave.} = -0.0147$ $\sigma = 0.0004$ Table 32 : Sensitivity analysis results, $VLE = VLE_{nominal} - 1\% VLE_{nominal}$

In the three cases studied, the interaction parameter varied with temperature when one of the experimental variable was modified. However, the standard deviation calculated for these tests is one order of magnitude smaller than the one obtained for the experimental results for a given mixture and composition, i.e. 0.0004 vs 0.003.

This would indicate that the temperature variation of f_{12} observed experimentally is not only attributable to experimental error but also to a temperature dependency of f_{12} .

The sensitivity of the method used to obtain the interaction parameter, as seen in Table 25, underlines the need to utilize very accurate instrumentation and a precise experimental procedure if reliable results are to be obtained. Therefore, in order to minimize experimental bias in the final results, it seems essential to obtain numerous experimental measurements of f_{12} . In this report, the average values of f_{12} are presented as a final result i.e. Table 23. If the temperature and/or composition dependency are to be measured it will be required to repeat the tests, in order to have an acceptable level of uncertainty in the results.

8.0 CONCLUSION

CRIQ has constructed a vapor-liquid equilibrium apparatus in order to determine refrigerant properties by measuring their bubble point. From this experimental data, calculations of the parameters required by the Carnahan-Starling-Desantis equation of state can be performed. The resulting parameters allow the various state properties to be calculated.

A total of seven pure substances and mixtures were tested in the CRIQ apparatus, as listed below :

PURE

R-22
R-114
R-142b
R-152a

MIXTURE

R-22/R-114
R-22/R-142b
R-22/R-152a

The experimental results lead to values of the " f_{12} " parameter that differed from those obtained by other workers [7]. However, given the uncertainty on the results these differences are not significant. A sensitivity analysis on the " f_{12} " parameter showed the sensitivity of the method used to determine this parameter. The pressure measurement uncertainty has the greatest effect on the interaction parameter f_{12} since a $\pm 1\%$ change in pressure lead to a $\pm 25\%$ variation in f_{12} .

The next step in this work will be to increase the VLE apparatus precision by installing new high accuracy pressure gages. Following this, a study of ternary mixtures and measurement of their state properties would be appropriate since the industry is also looking toward these substances as possible drop in substitutes for the banned CFCs.

9.0 REFERENCES

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- [2] Carnahan, N.F., and Starling, K.E., J. Chem. Phys., 51, 635 (1969).
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- [6] Private communications with Dr. Graham Morrison, Thermophysics Division, National Bureau of Standards.
- [7] McLinden, M.O., National Bureau of Standard, O.V. 745, Private communication.
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APPENDIX A

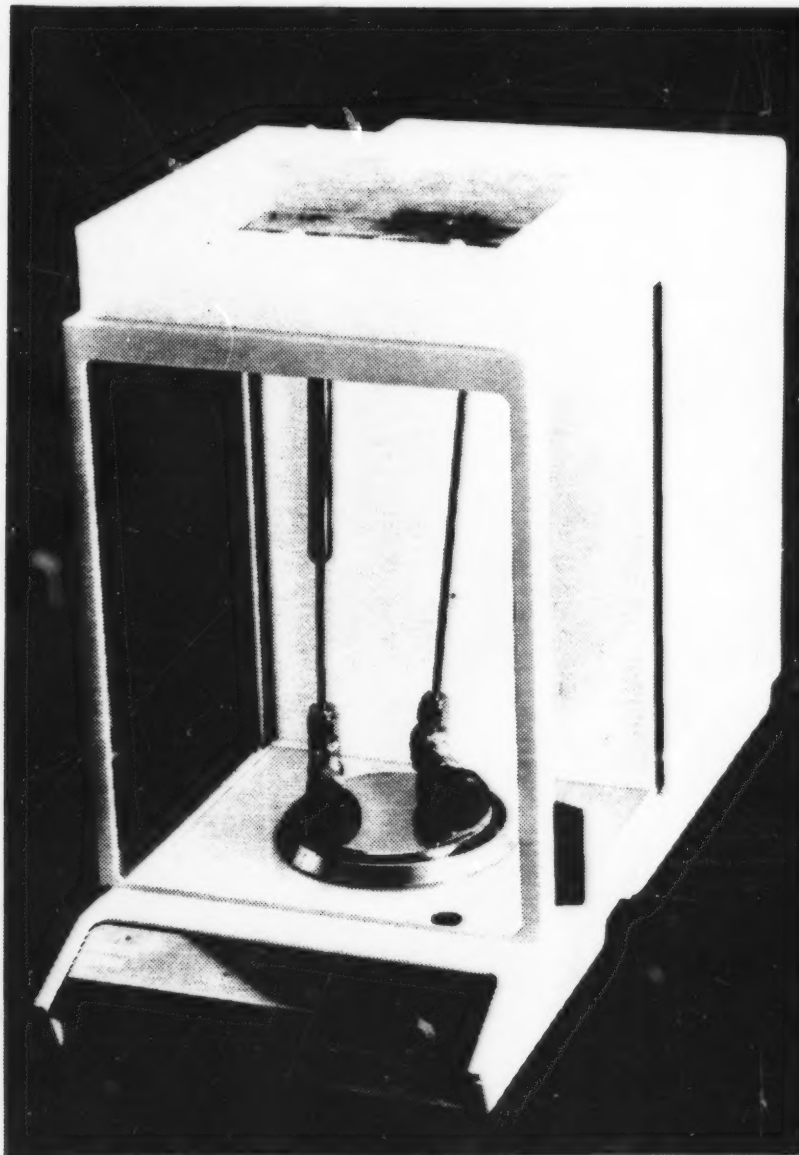


Figure 24 : Precision scale, used to determine sample weight, with preparation tube



Figure 25 : Set up used to prepare a mixture sample with two tubes connected.

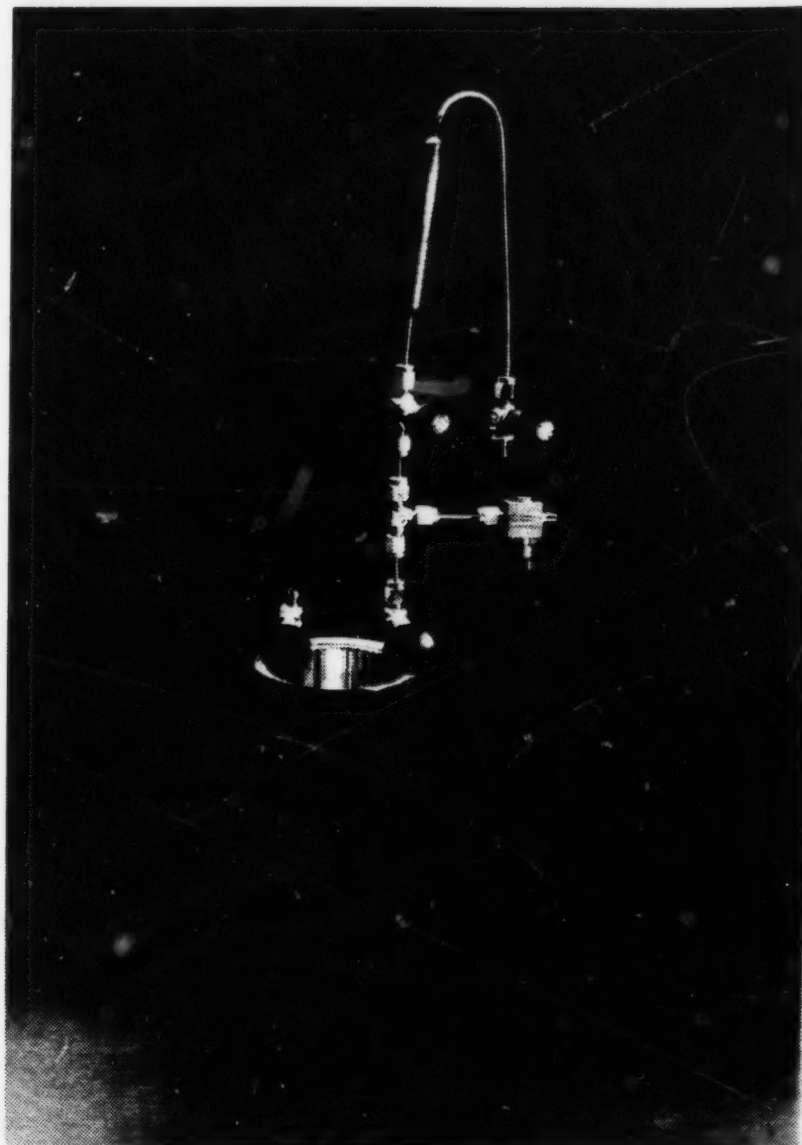


Figure 26 : Cryogenic pumping of the mixture sample into one of the two preparation tubes.

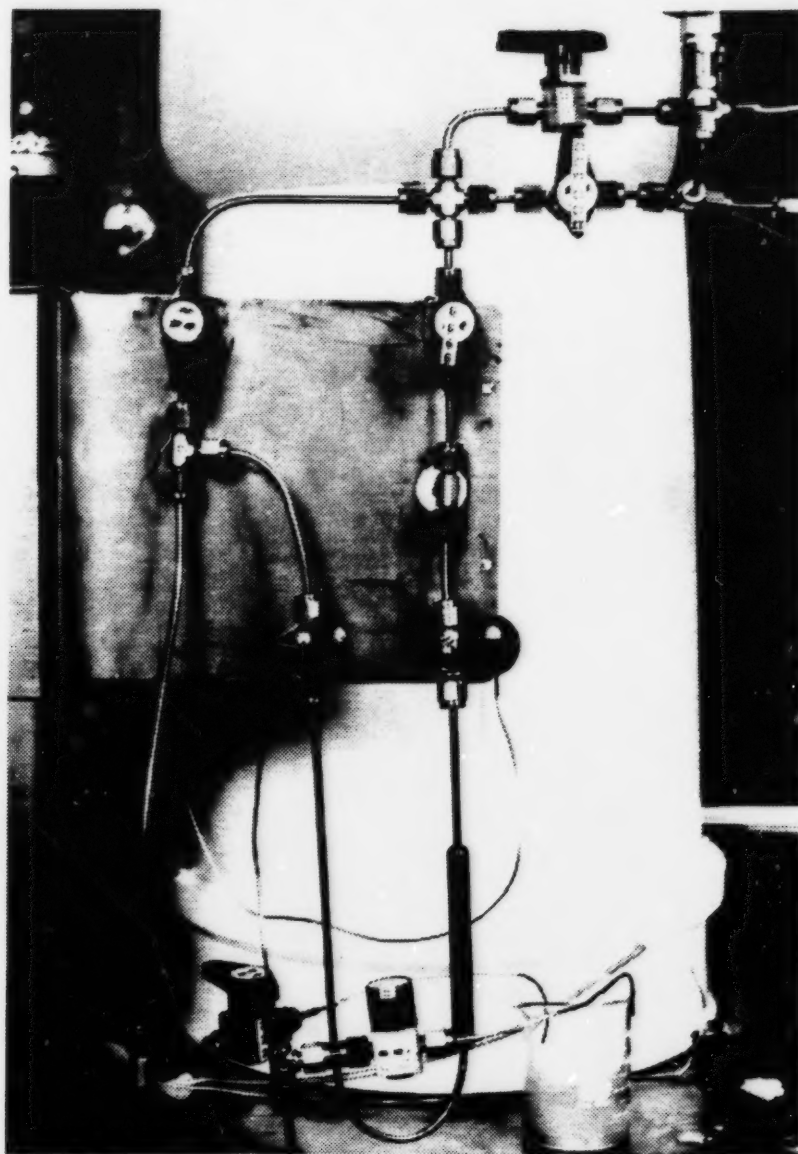


Figure 27 : Preparation tube installed on the VLE apparatus (between valves 2 and 3)

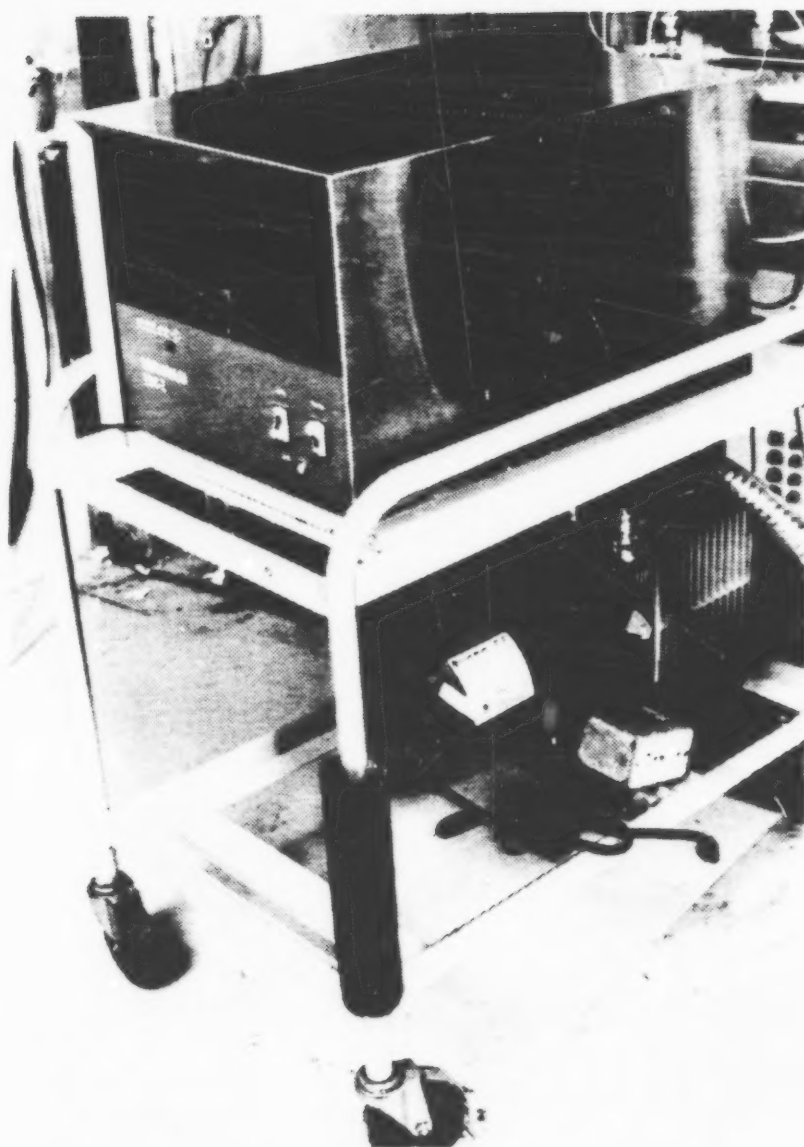


Figure 28 : Vacuum pump used to evacuate the apparatus and the NESTLAB bath cooler.

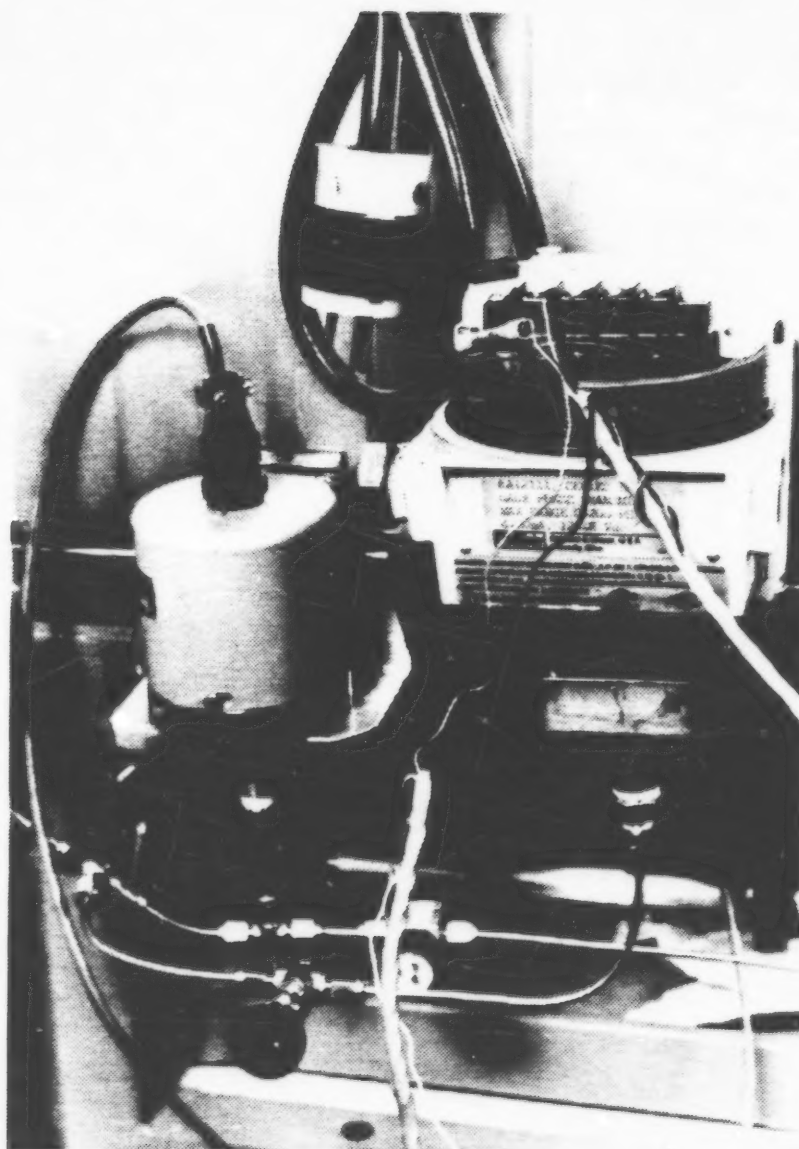


Figure 29 : Bailey pressure gage.

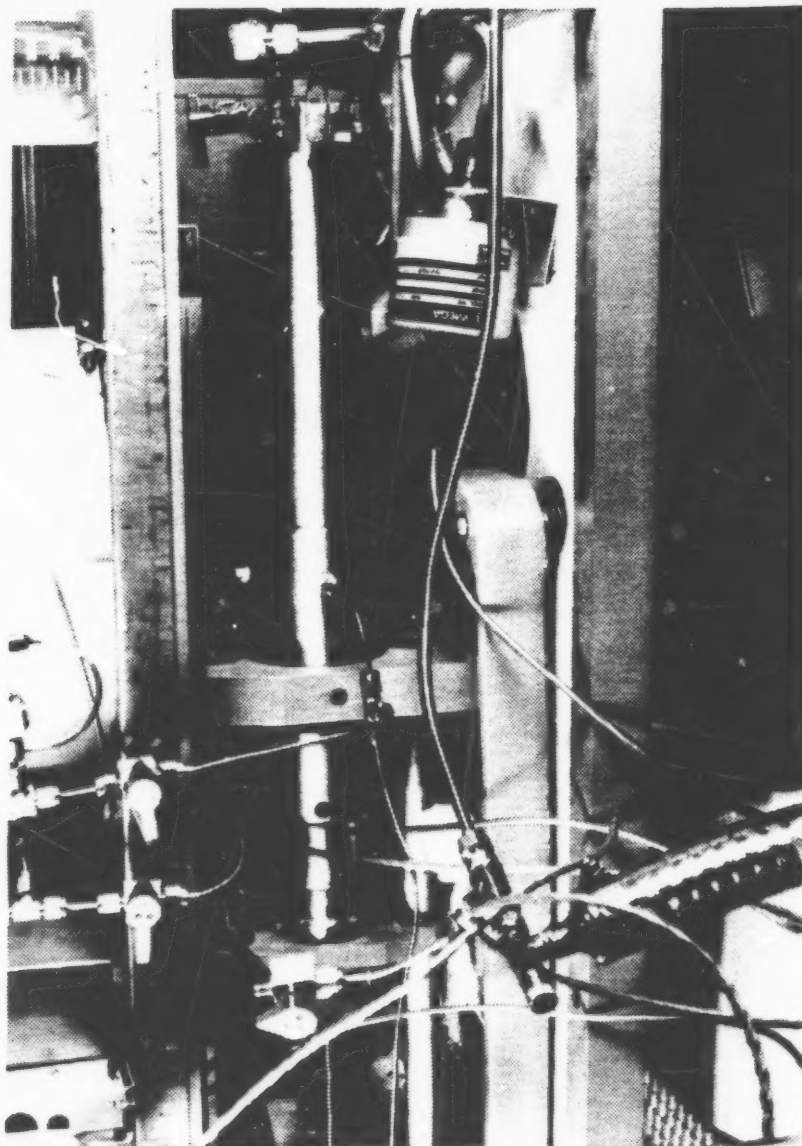


Figure 30: Manual mercury pump used to pressurize the refrigerant sample.

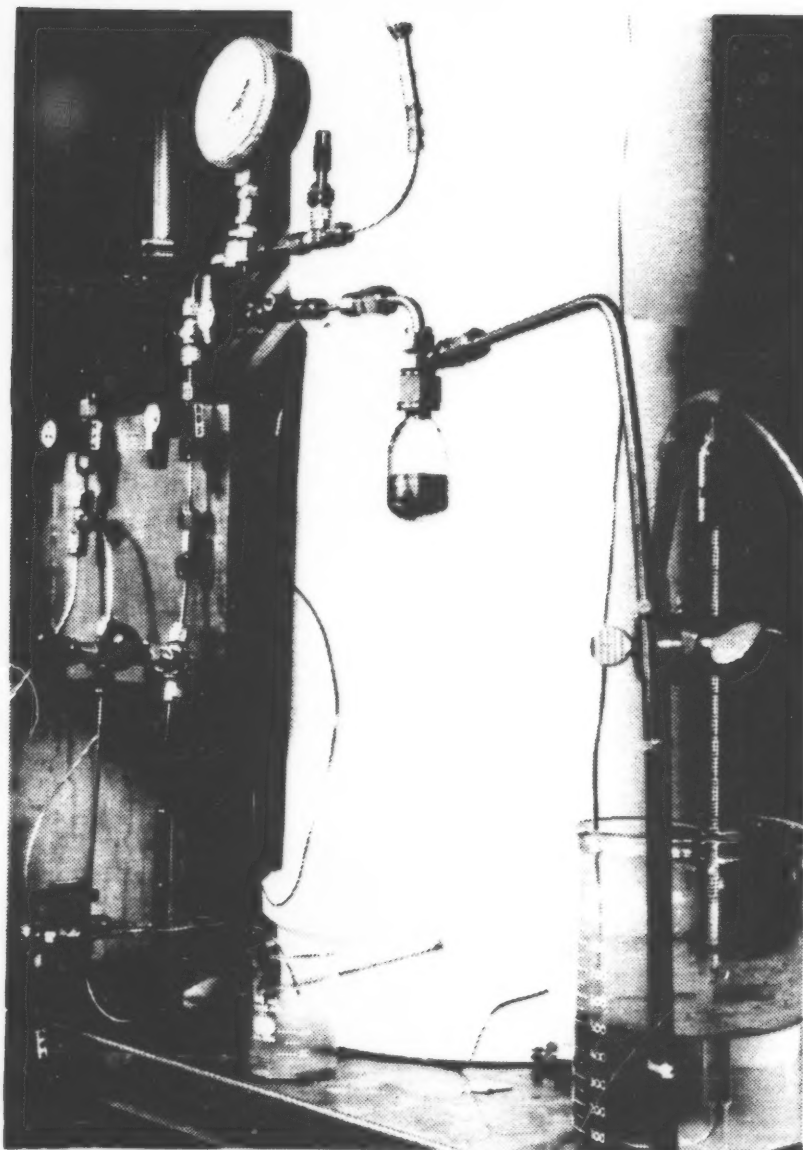


Figure 31: Graduated cylinder used to recuperate refrigerant gas left over in the lines (shown with mercury traps).

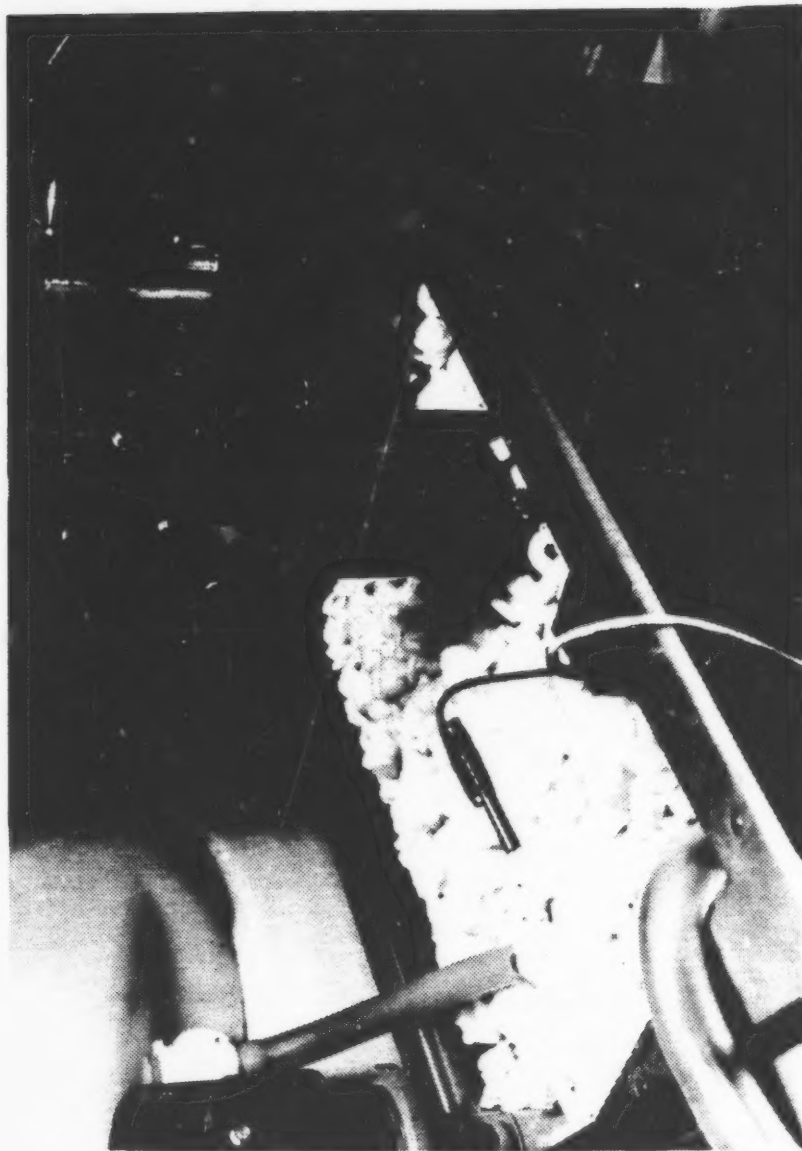


Figure 32 : Digital micrometer used to measure the meniscus of the liquid and mercury in the sapphire tube.

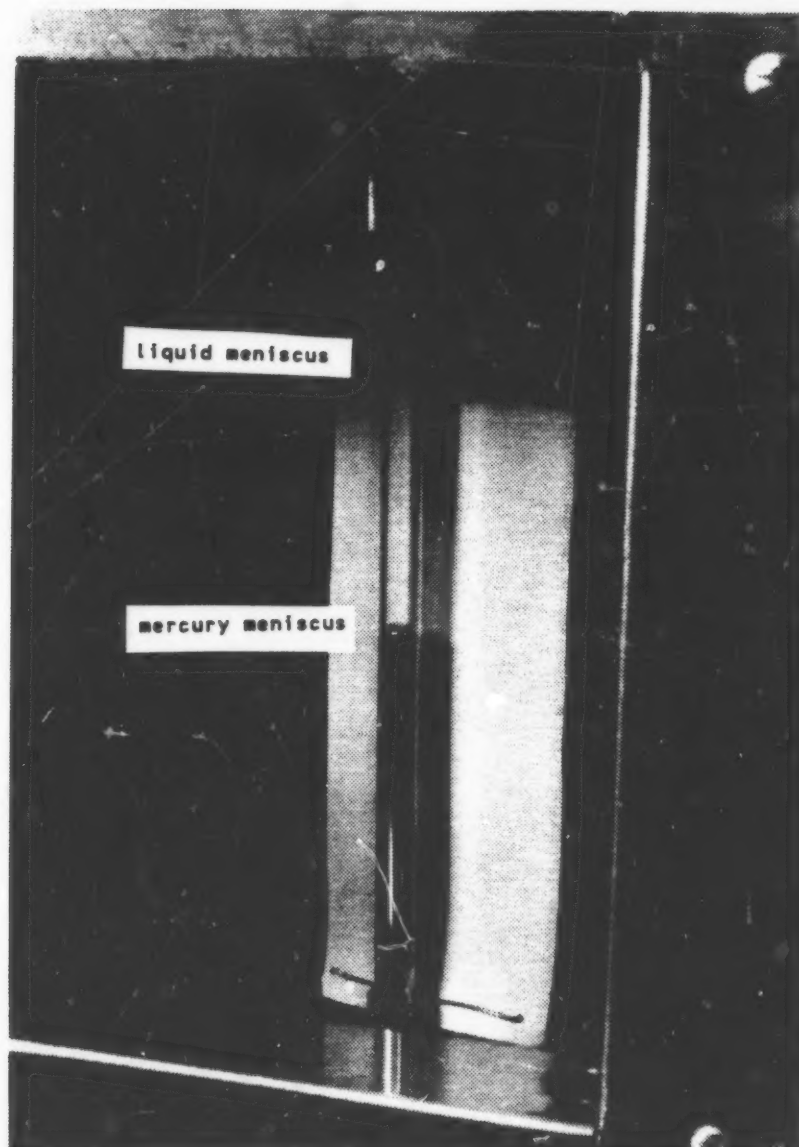


Figure 33 : Sapphire tube with a refrigerant sample. The mercury and liquid meniscus are clearly visible along with the small vapor portion left in the tube.

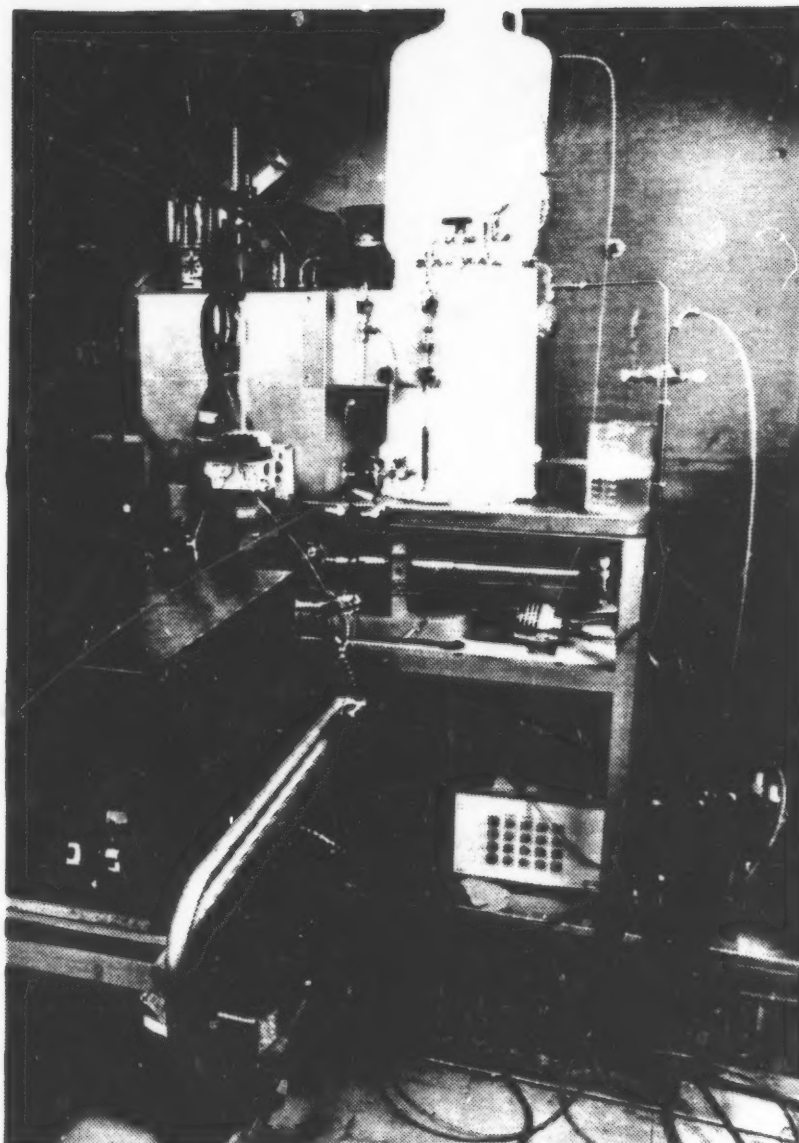


Figure 34 : Global view of the VLE apparatus.